Magnetic state of plutonium ion in metallic Pu and its compounds

A.O. Shorikov,[1] A.V. Lukoyanov,[1,2] M.A. Korotin,[1] and V.I. Anisimov[1]

[1] *Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-170, Russia*
[2] *Ural State Technical University-UPI, 620002 Yekaterinburg, Russia*

(Dated: February 2, 2008)

By LDA+U method with spin-orbit coupling (LDA+U+SO) the magnetic state and electronic structure have been investigated for plutonium in δ and α phases and for Pu compounds: PuN, $PuCoGa_5$, $PuRh_2$, $PuSi_2$, PuTe, and PuSb. For metallic plutonium in both phases in agreement with experiment a nonmagnetic ground state was found with Pu ions in f^6 configuration with zero values of spin, orbital, and total moments. This result is determined by a strong spin-orbit coupling in $5f$ shell that gives in LDA calculation a pronounced splitting of $5f$ states on $f^{5/2}$ and $f^{7/2}$ subbands. A Fermi level is in a pseudogap between them, so that $f^{5/2}$ subshell is already nearly completely filled with six electrons before Coulomb correlation effects were taken into account. The competition between spin-orbit coupling and exchange (Hund) interaction (favoring magnetic ground state) in $5f$ shell is so delicately balanced, that a small increase (less than 15%) of exchange interaction parameter value from $J_H = 0.48$ eV obtained in constrain LDA calculation would result in a magnetic ground state with nonzero spin and orbital moment values. For Pu compounds investigated in the present work, predominantly f^6 configuration with nonzero magnetic moments was found in $PuCoGa_5$, $PuSi_2$, and PuTe, while PuN, $PuRh_2$, and PuSb have f^5 configuration with sizeable magnetic moment values. Whereas pure jj coupling scheme was found to be valid for metallic plutonium, intermediate coupling scheme is needed to describe $5f$ shell in Pu compounds. The results of our calculations show that exchange interaction term in the Hamiltonian must be treated in a general matrix form for Pu and its compounds.

PACS numbers: 71.27.+a, 71.70.-d, 71.20.-b

I. INTRODUCTION

In actinide elements Coulomb interaction of $5f$ electrons is of the same order as a band width and spin-orbit coupling. Their interplay results in a complicated physics of $5f$ compounds[1] where both theorists and experimentalists still have attractive plenty of work. Among other actinides, plutonium element seams to be most intriguing,[2,3] despite numerous works and 60 years passed since the Pu discovery.[4,5]

Electronic properties of plutonium show an exceptional example of the system with $5f$ electrons on the edge between localization and itinerancy.[3,6] Experimental work[7] gave jj coupling for Pu $5f$ electrons or an intermediate coupling close to jj type.[8] Theoretical model for intermediate coupling scheme was suggested for PuSb by Cooper *et al.*[9]

Many experiments have been carried out to shed light on plutonium electronic structure. For δ-plutonium, most investigated of all metallic Pu phases, photoemission spectroscopy (PES) revealed special features of valence band[10,11,12] in particular a sharp peak at the Fermi level. X-ray, high-resolution ultraviolet,[13] and resonant photoemission[14] spectroscopy measurements accompanied with Pu $4f$ core-level spectra show more localized character of $5f$ electrons in δ-Pu phase comparing with α phase. Sharp peak at the Fermi level is indicative of strong many-particle nature and heavy-fermion behavior of $5f$ electrons. The electron mass enhancement is usually characterized by the inferred Sommerfeld coefficient $\gamma = 50$ mJ mol^{-1} K^{-2} for δ-Pu[15] versus $\gamma = 17$ mJ mol^{-1} K^{-2} for α-Pu.[16] Phonon dispersions and elastic moduli of δ-Pu showed a number of anomalies,[17,18] including softening of the transverse [111] modes,[19] suggesting unusual electronic structure and phonon-electron interaction for $5f$ electrons in plutonium (modern calculation results[20] qualitatively predicted experimental data). No evidence for ordered or disordered magnetic moments in plutonium in both δ and α phases was found in experiments.[2,4,21]

Ab-initio calculations of the electronic structure for plutonium have been done by many authors.[22] Standard local density approximation (LDA)[23] as well as generalized gradient approximation (GGA)[24] have been implemented. Full-potential linearized augmented plain-wave method (FLAPW) with GGA-correction and Gaussian-type orbitals-fitting function (LCGTO-FF) methods were used to reproduce zero-pressure experimental volumes and bulk module of Pu in the row of all actinides.[25] The obtained results show better agreement with experiment than, for example, LMTO-GGA method[26] but fails handling with Pu. Even with proper second variational approach to $6p$ states,[27] experimental volume of δ-Pu is still unattainable.[28] Another limitation of all these methods, as it was realized later, is inability to reproduce correctly electronic structure of plutonium due to neglect of Coulomb correlation effects.

To improve LDA approximation LDA+U method[29] was used, which explicitly takes into account strong Coulomb repulsion between $5f$ electrons by adding Hubbard-like term to the LDA Hamiltonian. The calculation of electronic structure for fcc-Pu by LDA+U method with GGA correction was performed in Ref. 30. Authors showed that for

the standard set of Slater integrals[31,32] and Coulomb parameter $U = 4.0$ eV significant improvement was achieved for calculated value of equilibrium volume comparing with experimental data. The resulting band structure suggests that Pu has five localized f electrons with substantial orbital and spin moments values. Another LSDA+U calculation with GGA correction gave similar results for different Coulomb parameter values.[33]

In contrast to experimental data, clearly showing nonmagnetic state of plutonium,[2,4,21] antiferromagnetic ground state was found for fcc-Pu in many calculations.[34,35,36,37] The fully relativistic spin-polarized calculation for fcc-plutonium phase was performed in Ref. 38. In another work (Ref. 39) it was shown that 'switching off' the hybridization makes better agreement with experiment for equilibrium volume in δ-Pu. For augmented plane waves basis (FLAPW),[40] Kutepov *et al.*[41] using the fully relativistic spin-polarized (RSP) method with GGA approximation obtained large orbital and spin moments. Antiferromagnetic ordered state was found lower in total energy of the system comparing with nonmagnetic one for both α- and δ-Pu phases.[41,42]

Another scheme was proposed by Eriksson *et al.*[43] Plutonium $5f$ electrons were divided into localized and delocalized ones. Self-interaction correction SIC-LSDA method[44,45,46,47] was used to calculate volumes and total energies of Pu ion in different configurations (with different valencies[44,48] of Pu ion). In contrast to experiments,[7] LS-coupled ground state was found to be lower in the total energy for any configuration of Pu ion[48] and f^3 configuration energetically preferable. For many binary Pu compounds SIC-LSDA calculations showed that experimental data are better described by the model of coexisting localized and delocalized electrons.[49] In particular, valency +5 was found for Pu ion in PuN and +3 in PuTe and PuSb.[49] Pu ion in plutonium dioxide by the same approach was obtained in f^4 configuration.[48,50] Similar hybrid schemes, disordered local moment (DLM) method[51] gave qualitative agreement with the photoemission spectrum for δ-Pu.[52]

Experiments suggest the presence of significant correlation effects for $5f$ electrons in plutonium. Dynamical Mean-Field Theory[53,54,55] (DMFT) is a powerful tool in studying such effects. Merging of LDA-based methods with DMFT gave a new calculation scheme – LDA+DMFT method.[56,57,58] Its application to plutonium problem[58,59] gave a better agreement with photoemission experiments and a double minimum curve of the total energy as a function of volume.

In this paper we present the results of calculation by LDA+U with spin-orbit coupling (LDA+U+SO) method of electronic structure and magnetic properties for metallic plutonium in α and δ phases and series of Pu compounds, namely PuN, $PuCoGa_5$, $PuRh_2$, $PuSi_2$, PuTe, and PuSb. Exchange interaction (spin polarization) term in the Hamiltonian was implemented in a general nondiagonal matrix form. This form is necessary for the correct description of $5f$ electrons for the case of jj coupling and intermediate coupling schemes which we have found to be valid in pure metallic Pu and its compounds. For metallic Pu in both δ and α phases, our calculations gave nonmagnetic f^6 ground state with six f electrons in fully occupied $j = 5/2$ sub-shell and spin, orbital, and total moments values equal to zero. This result is in agreement with experimental data for metallic plutonium,[21] but we have found magnetic ground state for all Pu-based compounds investigated in this work. For the present investigation we have chosen plutonium compounds with formal Pu ion valency +3 (PuN and PuSb) and +2 (PuTe) and also intermetallic compounds where valence state of Pu ion is not obviously defined. All calculated Pu-compounds possess magnetic moments on Pu ions with f^5, f^6 or mixed configurations. We were interested mainly in magnetic state problem and discussion of equilibrium volume and volume transition in plutonium and its compounds could be found elsewhere.[60] A strong competition between spin-orbit coupling and exchange interactions with a delicate balance was found to determine magnetic state of Pu and its compounds.

The organization of this paper is as follows. Sec. II describes LDA+U with spin-orbit coupling (LDA+U+SO) method used in the present work. In Sec. III results of calculations for metallic δ- and α-Pu phases are discussed in detail. Then Sec. IV describes applications of LDA+U+SO method to various plutonium compounds, including PuN in Subsec. IV A, $PuCoGa_5$ in Subsec. IV B, $PuRh_2$ in Subsec. IV C, $PuSi_2$ in Subsec. IV D, PuTe in Subsec. IV E, and PuSb in Subsec. IV F. Sec. V summarizes the paper.

II. METHOD

A strong spin-orbit coupling in actinides together with magnetism and Coulomb interactions rise a problem which was not present for materials without $5f$ electrons. For $3d$ and $4f$ elements compounds relatively weak spin-orbit coupling results in Russell-Saunders coupling (LS coupling) scheme with $\mathbf{S}$ and $\mathbf{L}$ operators well defined. Then the basis of LS orbitals, which are eigenfunctions of both spin $\mathbf{S}$ and orbital moment $\mathbf{L}$ operators, is a good choice. In this case it is possible to define quantization axis in the direction of spin moment vector so that occupation and potential matrices will be diagonal in spin variables. When spin-orbit coupling is stronger than exchange (Hund) interaction, jj coupling scheme is valid with a well defined total moment $\mathbf{J}$, but not spin $\mathbf{S}$ and orbital $\mathbf{L}$ moments. In this case, the basis of eigenfunctions of total moment operator $\{jm_j\}$ is a best choice. The matrix of spin-orbit coupling operator is diagonal in this basis but not the exchange interaction (spin-polarization) term in the Hamiltonian.

The situation for $5f$ electrons is more complicated. The strengths of spin-orbit coupling and exchange interaction are

comparable so that both aforementioned limits: LS coupling and jj coupling schemes are not valid and intermediate coupling scheme is needed to describe $5f$ shell in actinides. In this case occupation matrix is diagonal neither in $\{LS\}$, nor in $\{jm_j\}$ orbital basis and both terms in the Hamiltonian: spin-orbit coupling and exchange interaction, must be taken in a general nondiagonal matrix form.

In LDA+U method[29] the energy functional depends, in addition to the charge density $\rho(\mathbf{r})$, on the occupation matrix $n^{ss'}_{mm'}$ (LDA+U method in general nondiagonal in spin variables form was defined in Ref. 61):

$$E^{LDA+U}[\rho(\mathbf{r}),\{n\}] = E^{LDA}[\rho(\mathbf{r})] + E^{U}[\{n\}] - E_{dc}[\{n\}] \tag{1}$$

where $\rho(\mathbf{r})$ is the charge density and $E^{LDA}[\rho(\mathbf{r})]$ is the standard LDA functional. The occupation matrix is defined as:

$$n^{ss'}_{mm'} = -\frac{1}{\pi}\int^{E_F} ImG^{ss'}_{mm'}(E)dE \tag{2}$$

where $G^{ss'}_{mm'}(E) = \langle inlms \mid (E-\widehat{H}_{LDA+U})^{-1} \mid inlm's'\rangle$ are the elements of the Green function matrix in local orbital basis set (i – atomic index, n – principal quantum number, lm – orbital quantum numbers, and s – spin index). In the present work this basis set was formed by LMT-orbitals from LMTO method.[62] In Eq. (1) Coulomb interaction energy $E^U[\{n\}]$ term is a function of occupancy matrix $n^{ss'}_{mm'}$:

$$\begin{gathered} E^U[\{n\}] = \tfrac{1}{2}\textstyle\sum_{\{m\},ss'}\{\langle m,m'' \mid V_{ee} \mid m',m'''\rangle n^{ss}_{mm'} n^{s's'}_{m''m'''} \\ -\langle m,m'' \mid V_{ee} \mid m''',m'\rangle) n^{ss'}_{mm'} n^{s's}_{m''m'''}\} \end{gathered} \tag{3}$$

where V_{ee} is the screened Coulomb interaction between the nl electrons. Finally, the last term in Eq. (1) correcting for double counting is a function of the total number of electrons in the spirit of LDA which is a functional of total charge density:

$$E_{dc}[\{n\}] = \frac{1}{2}UN(N-1) - \frac{1}{4}JN(N-2) \tag{4}$$

where $N = Tr(n^{ss'}_{mm'})$ is a total number of electrons in the nl shell. U and J are screened Coulomb and Hund exchange parameters which could be determined in constrain LDA calculations.[63,64] The latter (J) in this paper is everywhere denoted as J_H not to be confused with total moment operator J. The screened Coulomb interaction matrix elements $\langle m,m'' \mid V_{ee} \mid m',m'''\rangle$ could be expressed via parameters U and J_H (see Ref. 29).

The functional Eq. (1) defines the effective single-particle Hamiltonian with an orbital dependent potential added to the usual LDA potential:

$$\widehat{H}_{LDA+U} = \widehat{H}_{LDA} + \sum_{ms,m's'} \mid inlms\rangle V^{ss'}_{mm'} \langle inlm's'\mid \tag{5}$$

$$\begin{gathered} V^{ss'}_{mm'} = \delta_{ss'}\textstyle\sum_{m'',m'''}\{\langle m,m'' \mid V_{ee} \mid m',m'''\rangle n^{-s,-s}_{m''m'''} + \\ (\langle m,m'' \mid V_{ee} \mid m',m'''\rangle - \langle m,m'' \mid V_{ee} \mid m''',m'\rangle) n^{ss}_{m''m'''}\} - \\ (1-\delta_{ss'})\textstyle\sum_{m'',m'''}\langle m,m'' \mid V_{ee} \mid m''',m'\rangle) n^{s's}_{m''m'''} \\ -U(N-\tfrac{1}{2}) + \tfrac{1}{2}J(N-1). \end{gathered} \tag{6}$$

In this paper we used method abbreviated as LDA+U+SO which comprises non-diagonal in spin variables LDA+U Hamiltonian Eq. (6) with spin-orbit (SO) coupling realized on the base of TB-LMTO-ASA code:[62]

$$\begin{gathered} \widehat{H}_{LDA+U+SO} = \widehat{H}_{LDA+U} + \widehat{H}_{SO}, \\ \widehat{H}_{SO} = \lambda \cdot \widehat{\mathbf{L}} \cdot \widehat{\mathbf{S}}. \end{gathered} \tag{7}$$

In LS basis spin-orbit (SO) coupling matrix has diagonal $(H_{SO})^{s,s}_{m',m}$ as well as off-diagonal $(H_{SO})^{\uparrow,\downarrow}_{m',m}$ and $(H_{SO})^{\downarrow,\uparrow}_{m',m}$ non-zero matrix elements (in complex spherical harmonics):

$$(H_{SO})^{\uparrow,\downarrow}_{m',m} = \frac{\lambda}{2}\sqrt{(l+m)(l-m+1)}(\delta_{m',m-1})$$
$$(H_{SO})^{\downarrow,\uparrow}_{m',m} = \frac{\lambda}{2}\sqrt{(l+m)(l-m+1)}(\delta_{m'-1,m}) \quad (8)$$
$$(H_{SO})^{s,s}_{m',m} = \lambda m s \delta_{m',m}$$

where $s = +1/2, -1/2$.[65]

The exchange interaction is originally a part of the Coulomb interaction (a second term in Eq. (3)). In the case when spin moment operator **S** is well defined, so that density and potential matrices can be made diagonal in spin variables, it is convenient to define spin-polarized density and spin polarized potential. In a most general form exchange interaction allowing non-collinearity of the spin polarization in space was introduced in density functional theory[66] (DFT) by von Barth *et al.*[67,68] and used later in Ref. 69,70:

$$\{[-\nabla^2 + V_{ext}(r) + \int d^3r' n(r') \frac{e^2}{\mid r - r' \mid} + v_{xc}(r; n, \vec{m})]\sigma_o + \vec{b}_{xc}(r; n, \vec{m}) \cdot \vec{\sigma}\}\Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (9)$$

where $\Psi_i(r)$ are one-electron spinors, σ_i are Pauli matrices. Exchange-correlation potentials determined as variational derivatives over space charge density $n(r)$ or magnetization vector $\vec{m}(r)$ are:

$$v_{xc}(r) = \frac{\delta E_{xc}[n, \vec{m}]}{\delta n(r)}, \quad \vec{b}_{xc}(r) = \frac{\delta E_{xc}[n, \vec{m}]}{\delta \vec{m}(r)} = \frac{\delta E_{xc}[n, m]}{\delta m}\hat{m}(r). \quad (10)$$

The exchange interaction is described here by the local magnetic field $\vec{b}_{xc}$ which acts on all orbitals in the same way. The potential matrix in LS basis for this field is diagonal in spin variables if quantization axis is chosen along direction of $\vec{b}_{xc}$.

A strong spin-orbit coupling in $5f$ shell produces an occupation matrix Eq. (2) and the corresponding potential matrix Eq. (6) which can not be made diagonal in spin variables by rotation of the quantization axis. Such rotation must be done to the direction of the spin moment vector, so that only S_z components were present while S_x, S_y components (responsible for off-diagonal in spin variable terms in Hamiltonian) set to zero. This is possible in the case where LS coupling scheme is valid and spin moment operator **S** is well defined, which is true for $3d$ and $4f$ elements compounds, but not for $5f$ electrons of actinides. For later materials not LS coupling scheme is valid but jj coupling or intermediate coupling schemes where spin moment operator **S** is not well defined.

That means that the widely used[38,41] form of spin-polarized potential based on Local Spin Density Approximation (LSDA) can not be applied for actinides, because LSDA neglects off-diagonal in spin variables terms in both spin density and potential. Those terms appear due to spin-orbit coupling Eq. (8) and suppress spin moment formation while exchange (Hund) part of Coulomb interaction prefers fully spin-polarized state with diagonal in spin variables occupation and potential matrices. A competition between spin-orbit coupling and exchange interaction determines the magnetic state of $5f$ shell. Neglecting off-diagonal in spin variables potential terms in the methods using LSDA potential enhances the tendency to spin moment formation. (In Sec. III we show that neglecting off-diagonal in spin variables potential terms in LDA+U+SO method results in a very strong increase of calculated spin and orbital moment values.) This fact could explain why antiferromagnetic ground state with a large value of spin moment was obtained in fully relativistic spin-polarized method calculations[38,41] in disagreement with experimental data.[2,4,21]

III. METALLIC PLUTONIUM

A. δ phase of plutonium

Phase diagram of plutonium is the most complex of all elements.[71] Of especial interest is fcc δ phase of Pu (a = 4.636 Å). A phase transition from δ- phase to low-temperature monoclinic α-plutonium phase (a = 6.183 Å, b = 4.824 Å, c = 10.973 Å, and β = 101.79°) is accompanied with a very large (19%) volume contraction. In the present work we were interested in the problem of magnetic state for Pu metal in α and δ phases.

In the LDA+U calculation scheme the values of direct (U) and exchange (J_H) Coulomb parameters must be determined as a first step of calculation procedure. It can be done in *ab-initio* way via constrain LDA calculations.[63,64] In our calculations Hund exchange parameter J_H was found to be J_H = 0.48 eV, much smaller than the value used in

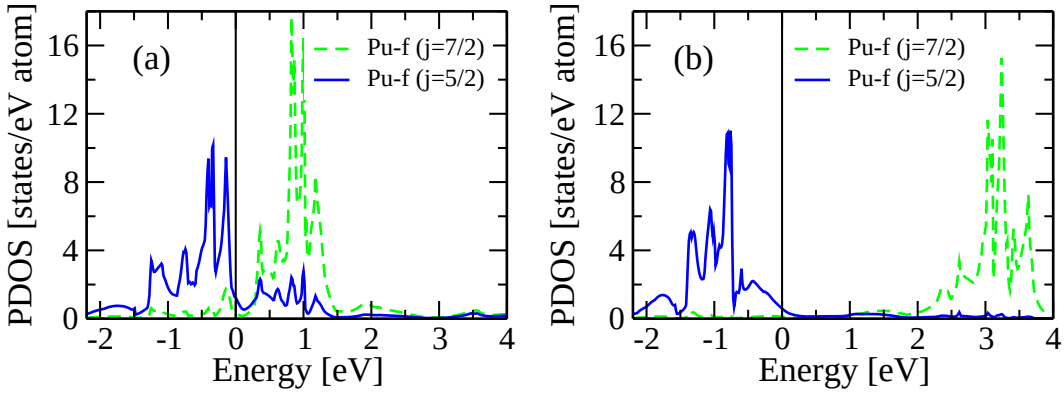

FIG. 1: Partial $f^{5/2}$ and $f^{7/2}$ contributions to $5f$ band densities of states of δ-plutonium calculated with LDA (a) and LDA+U+SO method (b).

previous LDA+U studies.[32] Coulomb repulsion parameter value $U = 3.84$ eV was obtained in a good agreement with previously used $U = 4$ eV.[20,30,59,72,73,74] Coulomb interaction parameters describe a *screened* Coulomb interaction between $5f$ electrons and hence crucially depend on the channels of screening taken into account in constrain LDA calculations. That is true for the direct Coulomb parameter U, but exchange Coulomb parameter J_H corresponds to the *difference* of interaction energy for the electrons pairs with the opposite and the same spin directions. As the screening process is defined by the charge but not spin state of the ion, the screening contribution is cancelled for exchange Coulomb interaction and parameter J_H does not depend on the screening channels choice. For example for $3d$ elements compounds, direct Coulomb interaction parameter varies from 8 eV for late transition metal oxides (NiO and CuO) to 3 eV for the beginning of the row (Ti and V oxides). At the same time exchange Coulomb parameter J_H is in the range of 0.85-0.95 eV for the whole $3d$ row. In our constrain LDA calculations we have found that J_H value is equal 0.48 eV within the accuracy 0.01 eV for both metallic Pu phases and for all plutonium compounds investigated in the present work.

In our constrain LDA calculations it was supposed that f shell is screened only by s, p, and d electrons, so that $5f$ electrons were considered to be completely localized and not participating in the screening. LDA calculations with spin-orbit coupling taken into account show (Fig. 1(a)) well separated subbands corresponding to the total moment values $j = 5/2$ and $j = 7/2$ with the Fermi level crossing the top of $j = 5/2$ band. This splitting of $5f$ shell into nearly filled $f^{5/2}$ and empty $f^{7/2}$ subshells can justify an additional screening of $f^{5/2}$ electrons by $f^{7/2}$ orbitals. In the constrain LDA calculations with this screening channel taken into account, Coulomb parameter value was obtained as $U = 0.44$ eV.

Plutonium is considered to be on the border between completely localized $5f$ electrons of americium and itinerant nature of them for early actinides, so that both limits, completely localized and totally itinerant, are not appropriate for Pu $5f$ electrons. The correct value of U should be somewhere in between the values calculated in those two limits (3.84 eV without any f electrons participating in the screening and 0.44 eV for full $f^{7/2}$-screening). As an additional requirement to determine U value we have chosen an equality of the calculated equilibrium volume of fcc-Pu to the experimental value of δ phase (see Fig. 2). This requirement is fulfilled for $U = 2.5$ eV and we used this Coulomb interaction parameter value in LDA+U+SO calculations for metallic Pu in both α and δ phases and for all Pu compounds investigated in this work.

The LDA+U+SO calculations for metallic Pu in δ phase gave a nonmagnetic ground state with zero values of spin **S**, orbital **L**, and total **J** moments. The occupation matrix Eq. (2) has six eigenvalues close to unit (see in Table I the row corresponding to $J_H = 0.48$ eV) and is nearly diagonal in the $\{jm_j\}$ basis of eigenfunctions of total moment **J**. That gives a f^6 configuration of Pu ion in jj coupling scheme. In the Fig. 1(b) the partial densities of states for $f^{5/2}$ and $f^{7/2}$ subshell orbitals are presented. In agreement with the occupation matrix analysis one can see nearly completely filled $f^{5/2}$ band with the Fermi level on the top of it and an empty $f^{7/2}$ band. The separation between the centers of these bands is ≈ 4 eV.

The origin of this nonmagnetic LDA+U+SO solution can be traced to the results of standard LDA calculations without Coulomb correlation correction but with spin-orbit coupling taken into account (see Fig. 1(a)). The $5f$ band is split by spin-orbit coupling into well pronounced $f^{5/2}$ and $f^{7/2}$ bands with a separation between their centers $\approx$ 1.5 eV. Fermi level is in the pseudogap between subbands closer to the top of $f^{5/2}$ band. Comparing Fig. 1(a) and Fig. 1(b) one can see that taking into account Coulomb correlations via LDA+U correction potential (Eq. 6) does not change qualitatively the band structure, only the separation between subbands increases from 1.5 eV to 4 eV

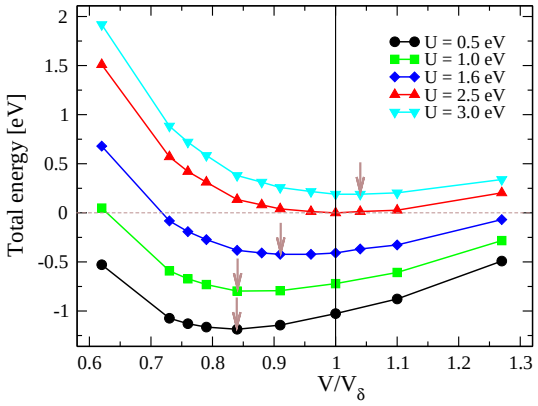

FIG. 2: Total energy as a function of volume for fcc-Pu calculated with various Coulomb parameter U values (V_δ corresponds to experimental volume value for Pu in δ phase). Arrows indicate minima of the curves giving equilibrium volume values. Calculated equilibrium volume is equal to experimental value for the curve with $U = 2.5$ eV.

TABLE I: Electronic configuration of Pu ion $5f$ shell in δ-plutonium calculated with LDA+U+SO method ($U = 2.5$ eV) for various values of Hund exchange parameter J_H. The largest values of occupation matrices off-diagonal elements (OD) in $\{LS\}$ and $\{jm_j\}$ basis sets are given in the second and third columns. The seven largest eigenvalues of occupation matrix are presented from fourth to tenth columns. Columns from eleven to thirteen show the calculated values for spin (S), orbital (L), and total (J) moments.[75] Last four columns contain partial contributions of f^5 and f^6 configurations and types of coupling for $5f$ shell of plutonium ion (see the text for explanations).

J_H, eV	OD$_{\{LS\}}$	OD$_{\{jm_j\}}$	largest eigenvalues							S	L	J	f^5	f^6	jj	LS
0.40	0.431	0.022	0.041	0.885	0.885	0.910	0.910	0.910	0.910	0	0	0	0	1.00	1.00	0.00
0.43	0.432	0.021	0.041	0.886	0.886	0.911	0.911	0.911	0.911	0	0	0	0	1.00	1.00	0.00
0.48	0.433	0.008	0.040	0.889	0.889	0.912	0.912	0.912	0.912	0	0	0	0	1.00	1.00	0.00
0.49	0.435	0.019	0.040	0.889	0.890	0.912	0.912	0.913	0.914	0.083	0.099	0.016	0.01	0.99	0.97	0.03
0.50	0.433	0.127	0.041	0.880	0.884	0.909	0.918	0.918	0.925	0.582	0.692	0.110	0.04	0.96	0.81	0.19
0.55	0.412	0.279	0.045	0.838	0.884	0.912	0.929	0.938	0.945	1.369	1.640	0.271	0.11	0.89	0.54	0.46
0.60	0.392	0.346	0.050	0.823	0.888	0.916	0.935	0.949	0.956	1.746	2.064	0.318	0.13	0.87	0.41	0.59

TABLE II: Electronic configuration of Pu ion in δ-plutonium calculated with LDA+U+SO method as a function of the $5f$ band shift value Δ. (Notations are the same as for Table I.)

Δ, eV	OD$_{\{LS\}}$	OD$_{\{jm_j\}}$	largest eigenvalues							S	L	J	f^5	f^6	jj	LS
0	0.433	0.008	0.040	0.889	0.889	0.912	0.912	0.912	0.912	0	0	0	0	1.00	1.00	0.00
0.14	0.431	0.012	0.040	0.879	0.879	0.906	0.906	0.906	0.906	0.023	0.029	0.006	0	1.00	0.99	0.01
0.27	0.431	0.044	0.040	0.864	0.866	0.897	0.900	0.903	0.905	0.210	0.286	0.076	0.03	0.97	0.93	0.07
0.41	0.427	0.188	0.042	0.642	0.865	0.919	0.919	0.934	0.942	0.920	1.700	0.780	0.31	0.79	0.70	0.30
0.82	0.432	0.256	0.043	0.254	0.910	0.924	0.942	0.954	0.959	1.316	3.040	1.724	0.69	0.31	0.56	0.44
1.36	0.419	0.256	0.040	0.086	0.886	0.886	0.938	0.947	0.962	1.378	3.609	2.231	0.89	0.11	0.53	0.47

according to the value of $U = 2.5$ eV. Another effect of Coulomb interaction is nearly pure orbital character of $f^{5/2}$ and $f^{7/2}$ bands in LDA+U+SO calculations comparing with a significant admixture of $f^{5/2}$ orbitals to the nominally $f^{7/2}$ band and vice versa in the LDA results (Fig. 1(a)). One can say, that nonmagnetic $J_H = 0$ solution with $f^{5/2}$ subshell filled with six electrons and empty $f^{7/2}$ band is already 'preformed' in LDA. Role of Coulomb correlations in LDA+U method is to make it more pronounced with a pure orbital nature of the bands and increased energy separation between them.

Photoemission spectroscopy is a direct tool for investigating electronic structure. Total density of states obtained in our LDA+U+SO study were multiplied with the Fermi function corresponding to the temperature of experiment and broadened with 0.2 eV Lorentian to account for the instrumental resolution (see Fig. 3). With the exception

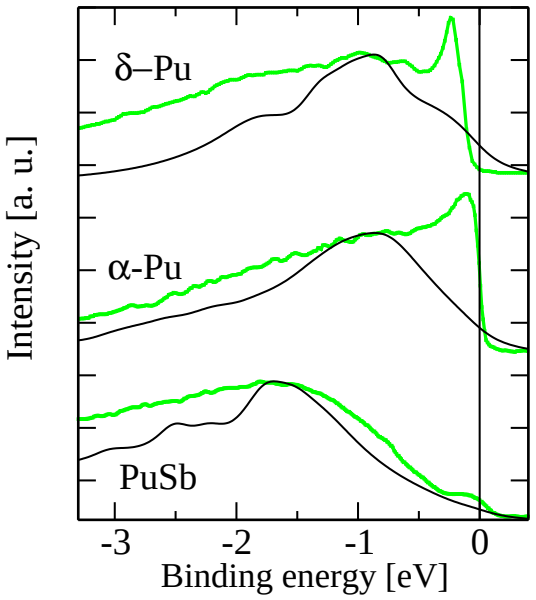

FIG. 3: Experimental (PES spectra for δ- and α-plutonium with $h\nu = 41$ eV and T = 80 K[10] and angle-integrated PES for PuSb at 15 K[125]) and calculated (thin line) photoemission spectra for metallic Pu in δ and α phases and for PuSb.

of the sharp peak near the Fermi level an overall agreement between experimental and calculated spectra for δ-Pu is satisfactory. This peak is usually considered as a sign of strong many-body effects, which can be described by Dynamical Mean-Field Theory[53,54,55] (DMFT) (see Ref. 58,59) but not by static mean-field approximation which is a basis of LDA+U method. However, LDA+U can reproduce the lower and upper Hubbard bands, on which partially filled f band is split by Coulomb interaction. Indeed the peak in experimental spectrum at ≈ 1 eV corresponding to the lower Hubbard band is well described by the calculated spectrum.

Our results are in agreement with experimental data showing the absence of ordered or disordered magnetic moments for plutonium in both δ and α phases.[2,4,21] However, all previous electronic structure calculations gave a magnetic (usually antiferromagnetic) state lower in energy than a nonmagnetic state. To clarify this problem we have carried out an investigation of the stability of our nonmagnetic ground state to the parameters of the calculations. The influence on it of the different approximations for exchange interaction and spin-orbit coupling terms in the Hamiltonian was investigated as well.

As a first step we have varied the value of exchange Coulomb parameter J_H around $J_H = 0.48$ eV value obtained in our constrained LDA calculations. In Table I the results of LDA+U+SO calculations with J_H values in the range from 0.40 eV till 0.60 eV are presented. One can see that even 15% increasing of J_H value is enough to result in a magnetic ground state with a sizable values of spin and orbital moments. However, the total moment value remains very small, less than 0.3 μ_B.

In addition to moment values, we show in the Table I values of the largest off-diagonal elements of occupation matrix Eq. (2) in $\{LS\}$ and $\{jm_j\}$ basis. As one can see, for the value $J_H = 0.48$ eV obtained in constrain LDA calculations, $\{jm_j\}$ basis is the most appropriate with largest off-diagonal elements values less than 0.01, while in $\{LS\}$ basis these values are very large (more than 0.4). That can be interpreted as a pure case of jj coupling with a well defined total moment ($\mathbf{J}$) but not spin ($\mathbf{S}$) and orbital ($\mathbf{L}$) moments. With increasing of J_H value the off-diagonal elements in $\{jm_j\}$ basis grow fast and for $J_H = 0.60$ eV become comparable with the off-diagonal elements in $\{LS\}$ basis making jj coupling scheme not valid any more. As the off-diagonal elements in $\{LS\}$ basis are still very large (≈ 0.4), the LS coupling scheme is also not appropriate and intermediate coupling scheme is needed to describe the magnetic solution.

The eigenvalues of occupation matrix Eq. (2) presented in Table I show six orbitals with occupancies close to unit for all values of J_H. Considering this one can conclude that Pu ion is predominantly in f^6 configuration in magnetic as well as in nonmagnetic state. Only nonmagnetic ground states corresponding to the values of Hund parameter $J_H \leq 0.48$ eV can be interpreted as a pure f^6 configuration in jj coupling scheme. Magnetic solutions for $J_H > 0.48$ eV correspond to predominantly f^6 configuration in intermediate coupling scheme.

In order to estimate, how close is a calculated state to one of the pure states (f^6 or f^5 configurations, in jj or LS coupling schemes) we propose the following simple formula using calculated values of spin (S), orbital (L), and total

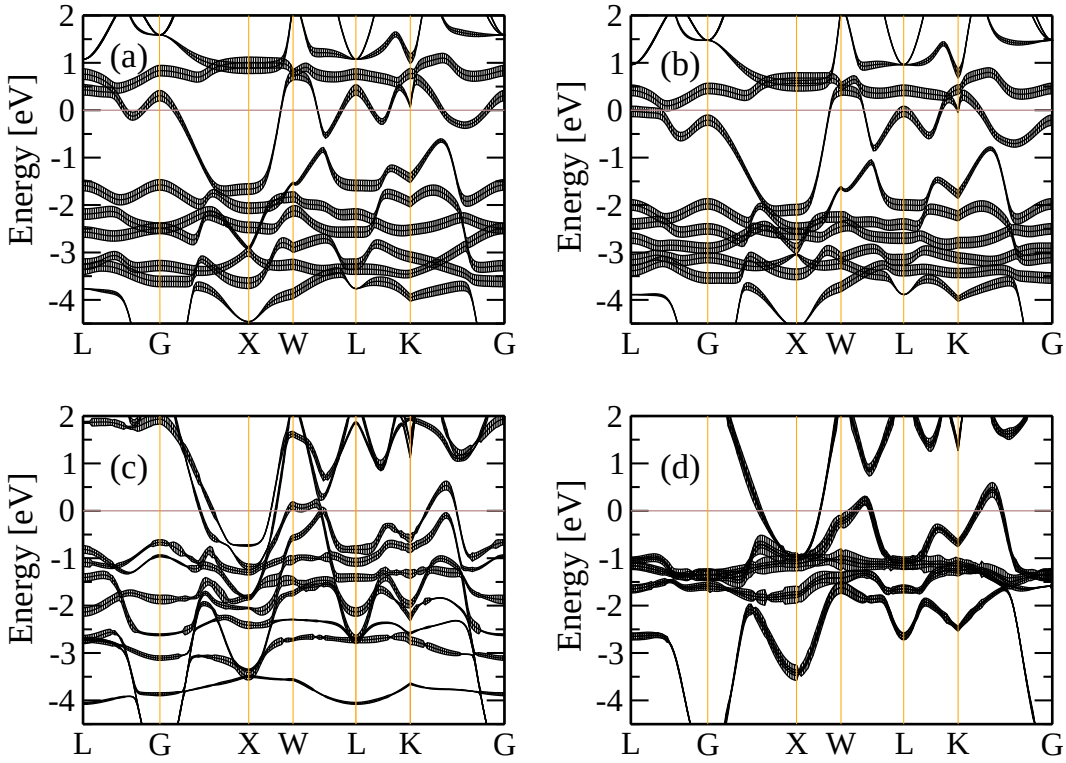

FIG. 4: (a) Band structure of δ-Pu (the width of the line shows the contribution of the $5f$ states to the particular band) from LSDA+U calculations with Coulomb parameters values $U = 4$ eV and $J_H = 0.85$ eV. (b) The same as (a) but for $J_H = 0.48$ eV. (c) The same as (a) but by LDA+U+SO method ($U = 4$ eV and $J_H = 0.85$ eV). (d) Same as (c) but for $J_H = 0.48$ eV (see text).

TABLE III: Calculated values for spin, orbital and total moments from LDA+U+SO calculations with off-diagonal in spin variables elements in potential matrix (Eq. 6) set to zero. For comparison the results of LSDA and LSDA+U calculations are presented.[75]

Method	S	L	J
LDA+U+SO ($U = 2.5$ eV, $J_H = 0.48$ eV)	2.43	3.57	1.14
LSDA+U (Ref. 33)	2.50	3.70	1.20
LSDA+U (Ref. 59)	2.55	3.90	1.45
LDA+U+SO ($U = J_H = 0.48$ eV)	1.70	2.30	0.60
LSDA (Ref. 41)	2.04	1.75	0.29
LSDA (Ref. 33)	2.11	1.94	0.17
LSDA (Ref. 38)	2.25	2.40	0.15

(J) moments. Total moment value is the same in both coupling schemes (jj or LS): $J = 0$ for f^6 and $J = 5/2$ for f^5. If we have a mixed state $(1-x)\cdot f^6 + x\cdot f^5$ then x can be defined as $x = J/2.5$. Spin and orbital moment values for f^6 configuration are equal to: $S = 0$, $L = 0$ in jj coupling scheme and $S = 3$, $L = 3$ in LS coupling scheme. For f^5 configuration $S = 5/14 \approx 0.36$, $L = 20/7 \approx 2.86$ in jj coupling scheme and $S = 5/2$, $L = 5$ in LS coupling scheme. One can define a mixed coupling scheme with a contribution of jj coupling equal to y and of LS coupling correspondingly to $(1-y)$. In this scheme the calculated values of orbital and spin moment will be equal to

$$L = x\cdot(2.86\cdot y + 5\cdot(1-y)) + (1-x)\cdot(0\cdot y + 3\cdot(1-y)) \quad (11)$$

$$S = x\cdot(0.36\cdot y + 2.5\cdot(1-y)) + (1-x)\cdot(0\cdot y + 3\cdot(1-y) \quad (12)$$

These formulas allow to determine the coefficient y.

The values of coefficients x and y calculated in this way are shown in Table I. For values of Hund parameter $J_H \leq 0.48$ eV they correspond to the pure f^6 configuration in 100% jj coupling scheme. With increase of J_H value

the contribution of LS coupling increases and for J_H close to 0.60 eV both coupling scheme gave approximately equal contribution demonstrating a clear case of intermediate coupling scheme. However the configuration is still predominantly f^6 with not more than 10% admixture of f^5.

Not only the strength of exchange interaction parameter J_H is crucial for the magnetism of the $5f$ shell in metallic Pu. The Fermi level is on the top of $f^{5/2}$ band (see Fig. 1(a)) and a small shift of relative energy position of $5f$ and other states can lead to redistribution of electrons between $5f$ and *spd*-bands and hence change the f configuration and magnetic state of Pu ion. To investigate this effect we run the LDA+U+SO calculations with a constant positive potential Δ acting on $5f$ electrons, which should result in a charge flow from $5f$ bands to *spd*-bands (see Table II). Already relatively small value of the shift ($\Delta = 0.41$ eV) is enough to produce a well pronounced magnetic ground state with a sizable admixture of f^5 configuration (around one third). For the shift value equal to 1.36 eV the Pu ion is in a pure f^5 configuration with a very large values of spin, orbital, and total moments.

These constrain LDA+U+SO calculations demonstrate that a relative position of $5f$ and other bands is of great importance for the resulting configuration and magnetic state of Pu ion. Later we will show that in all investigated in this work plutonium compounds we obtained a magnetic ground state in contrast to the nonmagnetic one for metallic Pu.

In order to study the influence of the different approximations for exchange interaction term in the Hamiltonian we have performed at first LSDA+U (electron density and LDA potential were used in spin-polarized forms) calculations with the same Coulomb interaction parameters values as in Ref. 30 (exchange parameter value corresponds to $J_H = 0.85$ eV[32] and $U = 4$ eV). In this calculation the strong magnetic state with a configuration close to f^5 was obtained in agreement with results of Ref. 30. The $5f$ bands dispersion is presented in Fig. 4(a) (the width of the band curve is proportional to the contribution of $5f$ states to the band). It agrees well with the corresponding figure in Ref. 30. Decreasing of the Coulomb exchange parameter value J_H from 0.85 eV to the value 0.48 eV (obtained in our constrain LDA calculations) gave still magnetic solution with spin $S = 2.5$ but the $5f$ configuration is now more close to f^6 than to f^5 (the Fermi level (Fig. 4(b)) is now above the top of the band which was cut by the Fermi level in Fig. 4(a)). As a next step we have used LDA+U+SO calculation scheme (1-8) with non-spin-polarized electron density and LDA potential but keeping Hund parameter $J_H = 0.85$ eV[30,32] (see Fig. 4(c)). In this calculation we have found magnetic ground state ($S = 2.5$, $L = 2.7$, and $J = 0.2$) with a configuration close to f^6. And only the calculation by LDA+U+SO with Coulomb exchange parameter value obtained in constrain LDA calculations ($J_H = 0.48$ eV) gave (see Fig. 4(d)) a nonmagnetic state with $S = 0$, $L = 0$, and $J = 0$.

In the Sec. II we have discussed that the use of spin-polarized potential based on LSDA is equivalent to neglecting off-diagonal in spin variables exchange potential terms and hence enhances the tendency to spin moment formation. To check this we have performed LDA+U+SO calculations with the off-diagonal in spin variables terms in LDA+U potential (Eq. 6) set to zero ($U = 2.5$ eV and $J_H = 0.48$ eV). As a result we indeed obtained a magnetic ground state (see Table III) which is close to the results of LSDA+U calculations.[33,59] To compare with the results of fully relativistic spin-polarized calculation we have performed LDA+U+SO calculations with the off-diagonal in spin variables terms in LDA+U potential (Eq. 6) set to zero using the value of Coulomb parameter $U = J_H = 0.48$ eV. In Ref. 76 it was shown that $U - J_H$ can be regarded as an effective Coulomb interaction parameter U_{eff} in LSDA+U calculations, so the choice of $U = J_H$ is equivalent to $U_{eff} = 0$. Such calculations gave solution with a large values of spin and orbital moments (see Table III) similar to LSDA results.

B. α phase of plutonium

A transition from δ to α phase can be described as a volume contraction on 19% and a monoclinic distortion of the fcc lattice. To separate the influence on the electronic structure and magnetic properties of the volume contraction and lattice distortion, we performed the LDA+U+SO calculation for fcc lattice with the volume per Pu atom corresponding to α phase. The result is the same nonmagnetic solution: $S = 0$, $L = 0$, and $J = 0$ in f^6 configuration as was obtained for δ phase. A variation of Hund parameter J_H has shown that for Pu in fcc-structure with the volume of α phase nonmagnetic solution is a little more stable than for δ phase volume (while in the latter case already 15% increase of J_H was enough to produce the magnetic state, for α phase volume 20% increase is needed).

LDA+U+SO calculation for real monoclinic crystal structure of α phase (see Fig. 5) also gave a nonmagnetic ground state with $S = 0$, $L = 0$, $J = 0$ in f^6 configuration. Comparing with the results for δ phase (Fig. 1) one can see that bands become more broad (Fig. 5(a)) due to the smaller volume and hence increased hybridization strength. Correspondingly $f^{5/2}$ and $f^{7/2}$ bands have a much more mixed character (a strong admixture of $f^{5/2}$ orbitals to the nominally $f^{7/2}$ band and vice versa) comparing with a more pure band character for δ phase (Fig. 1(a)). However, after taking into account Coulomb interaction in LDA+U+SO calculations (Fig. 5(b)) the band structure becomes very similar to the case of δ phase (Fig. 1(b)). $f^{5/2}$ and $f^{7/2}$ bands have now pure orbital character. $f^{5/2}$ band is nearly completely filled with the Fermi level on the top of it and an $f^{7/2}$ band is empty. The separation between the

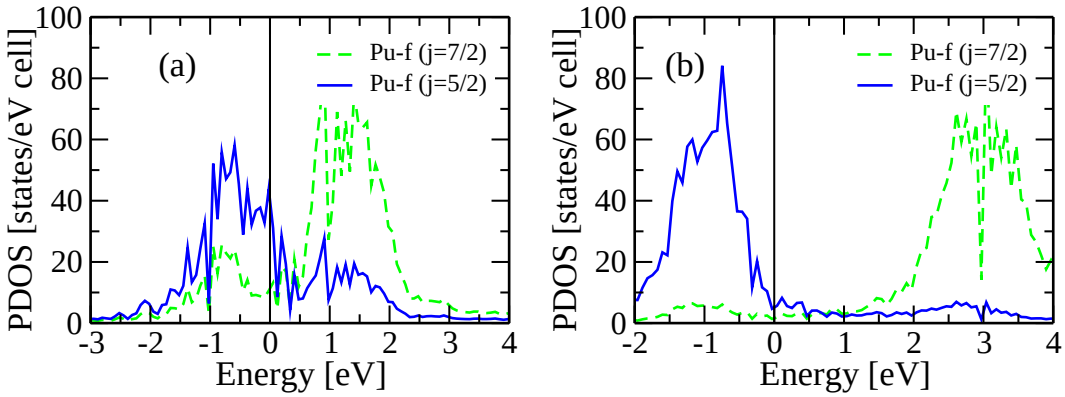

FIG. 5: Partial $f^{5/2}$ and $f^{7/2}$ contributions to $5f$ band densities of states of α plutonium calculated with LDA (a) and LDA+U+SO method (b).

TABLE IV: Electronic configuration of Pu ion in various plutonium compounds calculated with LDA+U+SO method. Notations are the same as for Table I.

Compound	$OD_{\{LS\}}$	$OD_{\{jm_j\}}$	largest eigenvalues							S	L	J	f^5	f^6	jj	LS
PuN	0.436	0.239	0.118	0.162	0.923	0.930	0.960	0.965	0.978	1.279	3.339	2.060	0.82	0.18	0.57	0.43
$PuCoGa_5$	0.426	0.226	0.029	0.796	0.883	0.897	0.922	0.939	0.941	1.144	1.594	0.450	0.18	0.82	0.62	0.38
$PuRh_2$	0.348	0.302	0.127	0.525	0.610	0.883	0.908	0.924	0.927	1.546	3.421	1.875	0.75	0.25	0.46	0.54
$PuSi_2$	0.441	0.142	0.070	0.907	0.916	0.939	0.949	0.960	0.962	0.692	0.829	0.137	0.05	0.95	0.77	0.23
PuTe	0.441	0.253	0.026	0.895	0.904	0.908	0.928	0.940	0.946	0.907	1.069	0.162	0.06	0.94	0.70	0.30
PuSb	0.453	0.320	0.046	0.127	0.959	0.961	0.973	0.981	0.982	1.583	3.650	2.067	0.83	0.17	0.44	0.56

centers of those bands is ≈ 4 eV.

The calculated photoemission spectra (see Fig. 3) is not very different from the corresponding curve for the δ phase except that it is more smooth and does not show high and lower energy shoulders. The sharp peak near the Fermi level which is stronger in experimental spectrum for the α phase than for δ phase spectrum is missing in the calculated spectrum as it was in the case for the δ phase. Again we expect that Dynamical Mean-Field Theory[53,54,55] (DMFT) (see Ref. 58,59) can solve this problem. But the peak in experimental spectrum at ≈ 1 eV corresponding to the lower Hubbard band is well described by the calculated spectrum.

As we have shown above, the calculations scheme presented here is different from the ones used in previous investigations of plutonium electronic structure and magnetic properties. A resulting nonmagnetic ground state (Pu ion in f^6 configuration with jj coupling scheme) was never obtained in any other calculations. In order to check validity of our method we have performed calculations for a series of Pu compounds. The main aim of this calculations was to investigate magnetic properties for these compounds and compare the results with the available experimental data.

IV. PLUTONIUM COMPOUNDS

A. PuN

Plutonium mononitride crystallizes in a *rock–salt*-type structure with $a = 4.905$ Å.[77] Neutron diffraction showed no long-range order and magnetic moments larger than 0.25 μ_B.[78] From the magnetic susceptibility and specific heat measurements an antiferromagnetic transition at $T_N = 13$ K was proposed.[79] According to another magnetic susceptibility curve, PuN is a Curie-Weiss paramagnet with $\mu_{eff} = 1.08\ \mu_B$.[80] Electronic structure of PuN was calculated in L(S)DA with and without relativistic correction.[81] SIC-LSDA method showed valency +5 to be energetically preferred in the model with partially localized $5f$ electrons of Pu ion.[49]

Fig. 6(a) and 6(b) show total and partial f density of states of PuN obtained in our LDA with spin-orbit coupling calculation (when the Coulomb interaction correction was 'switched off'). Nitrogen $2p$-states are strongly hybridized with Pu-f states and the Fermi level is located inside the $j = 5/2$ subband. While $j = 5/2$ and $j = 7/2$ subbands

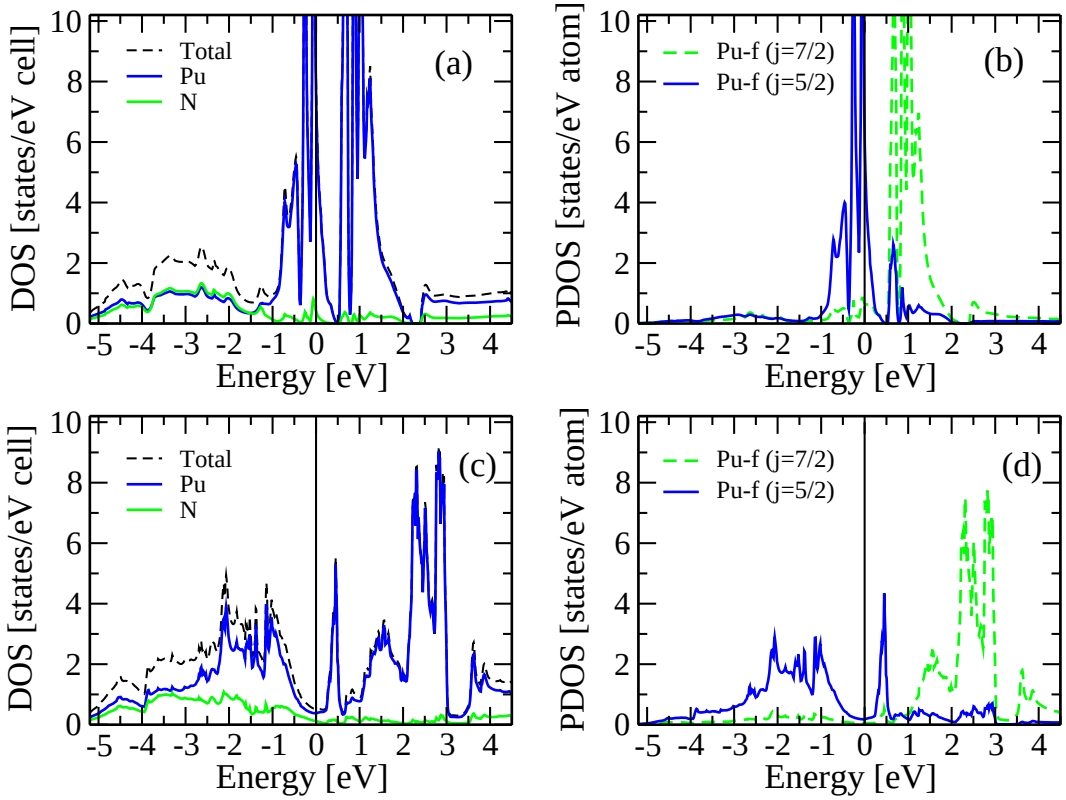

FIG. 6: (a) Total and partial densities of states of PuN calculated in LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuN from LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

TABLE V: Values of effective paramagnetic moments (in Bohr's magnetons μ_B) calculated from the total moment value J in jj and LS coupling schemes μ_{eff}^{LS} and μ_{eff}^{jj} and their weighted value μ_{eff}^{calc} in comparison with experimental data μ_{eff}^{exp} (see text).

Compound	J	jj	LS	μ_{eff}^{jj}	μ_{eff}^{LS}	μ_{eff}^{calc}	μ_{eff}^{exp}
PuN	2.060	0.57	0.43	2.16	0.72	1.54	1.08[80]
$PuCoGa_5$	0.450	0.62	0.38	0.69	0.23	0.52	0.68[82]
$PuRh_2$	1.875	0.46	0.54	1.99	0.66	1.27	0.88[98]
$PuSi_2$	0.137	0.77	0.23	0.34	0.11	0.23	0.54[100,102]
PuTe	0.162	0.70	0.30	0.37	0.12	0.30	–
PuSb	2.067	0.44	0.56	2.16	0.72	1.35	1.00[121]

are well separated from each other (see 6(b)), they do not have pure orbital character with a strong admixture of $j = 5/2$ states to the formally $j = 7/2$ subband. The results of LDA+U+SO calculation are presented in Fig. 6(c) and 6(d). In contrast to metallic Pu case Coulomb interaction correction not only has increased energy separation between $j = 5/2$ and $j = 7/2$ subbands, but also led to the splitting of $j = 5/2$ subband into occupied and empty states (see the peak of $j = 5/2$ character just above the Fermi energy on 6(d)). As this split-off band contain one electron per Pu ion, one can conclude that our results correspond to the configuration f^5 in agreement with formal Pu valency +3 in PuN.

In Table IV (the first row corresponds to PuN) the calculated values for spin, orbital and total moments are presented. The total moment $J = 2.218$ is close to an ideal value $j = 5/2$ for f^5 configuration. Five largest eigenvalues of the occupation matrix also show a well defined f^5 configuration. The analysis of occupation matrices off-diagonal elements show that in $\{jm_j\}$ basis the values of those elements are nearly two times smaller than the corresponding values for $\{LS\}$ basis. That corresponds to the intermediate coupling scheme closer to jj coupling. The analysis

based on the calculated values for spin, orbital, and total moments (see Eq. (12) in Sec. III A) gave 89% f^5 and 11% f^6 configuration with 57% of jj and 43% of LS couplings.

In order to compare our results with the experimental magnetic measurements data we should obtain the magnetic moment value using calculated values of spin (S), orbital (L), and total moments (J). In the cases when spin-orbit coupling is weak and Russell-Saunders coupling (LS coupling) scheme is valid with **S** and **L** operators well defined, this is a very simple task: total magnetic moment value can be calculated as:

$$M_{tot} = 2 \cdot S + L \tag{13}$$

However for strong spin-orbit coupling when jj or intermediate coupling schemes should be used, this problem becomes much more complicated. For the intermediate coupling scheme there is no general solution of this problem and for jj coupling it can be solved only for the free ions in pure configuration. An effective paramagnetic moment obtained from susceptibility measurements using Curie-Weiss law can be calculated as:

$$\mu_{eff} = g \cdot \sqrt{J \cdot (J+1))} \cdot \mu_B \tag{14}$$

The problem is to define Lande g-factor which can be calculated for pure f^5 and f^6 configurations in LS or jj coupling schemes. As for f^6 configuration total moment value $J = 0$, one need to calculate g-factor for f^5 configuration only. For ground state of f^5 configuration in jj coupling scheme Lande factor $g_{jj} = 6/7 \approx 0.86$. In LS coupling scheme its value is $g_{LS} = 2/7 \approx 0.29$. As the latter value is nearly three times larger than the former, g_{jj} and g_{LS} can give only an upper and lower limits of g-factor for the case of intermediate coupling.

In Table V the values of effective paramagnetic moments calculated using Eq. (14) are presented. In addition to μ_{eff}^{LS} and μ_{eff}^{jj} calculated using Lande factors g_{LS} and g_{jj} correspondingly, we have calculated their weighted value μ_{eff}^{calc} using relative weight of LS and jj coupling obtained from Eq. (12).

Results for PuN (the first row of the Table V) gave $\mu_{eff}^{calc} = 1.54\ \mu_B$ in a reasonable agreement with the experimental value $\mu_{eff}^{exp} = 1.08\ \mu_B$.

B. $PuCoGa_5$

Since first reported in 2002 by Sarrao *et al.*,[82] superconductor $PuCoGa_5$ has attracted a special attention being the first Pu-containing superconductor in well-known superconductor class of '115' materials.[83,84,85] Its superconducting temperature $T_c = 18.5$ K is an order of magnitude higher than for other '115' superconductors.[84,85] Specific heat coefficient value $\gamma = 77$ mJ mol^{-1} K^{-2} above T_C and Curie-Weiss behavior of magnetic susceptibility with $\mu_{eff} = 0.68\ \mu_B$ are indicative of unconventional superconductivity of $PuCoGa_5$.[82,86,87,88,89,90] Tanaka *et al.*[91] used periodic Anderson model to describe d-wave superconducting state of $PuCoGa_5$. Its isostructural counterpart $PuRhGa_5$ shows analogous properties but with the lower value of SC transition temperature $T_c = 8$ K.[92]

$PuCoGa_5$ crystallizes in tetragonal $P4/mmm$ space group with $a = 4.232$ Å and $c = 6.782$ Å.[82] Electronic structure calculation of $PuCoGa_5$ was performed in fully relativistic full-potential method of local orbitals.[93] In that work the paramagnetic state has a total energy value substantially higher than FM and AFM solutions.

The LDA calculation without spin-orbit coupling[83,94] showed the Fermi level crossing Pu $5f$ bands manifold without any splitting. Another calculation by relativistic LAPW method[95] gave Fermi surface analogous to CeMIn$_5$ series. Microscopic model for compounds with f ions in jj coupled state was extended to $PuCoGa_5$ in Ref. 96. Antiferromagnetic order was proposed in electronic structure calculation in Ref. 97. For our knowledge, in this work we report the first electronic structure calculation for $PuCoGa_5$ with Coulomb interactions taken into account beyond LDA or GGA approximations.

In PuN only $5f$-bands are present at the Fermi level while fully occupied N-p band is situated substantially lower (Fig. 6(a)). In contrast to that in $PuCoGa_5$ Co-d and Ga-p bands cross the Fermi level in addition to $5f$ bands of Pu (see Fig. 7(a)) so that $5f$ states contribute only one third to the of density of states value at the Fermi energy. This fact leads to a very complicated general band structure for this compound (Fig. 6(a)) but the partial $5f$ densities of state presented on Fig. 6(b) shows well pronounced $f^{5/2}$ and $f^{7/2}$ subbands with ≈ 1.5 eV separation between them. This picture is very close to the results for δ phase of metallic Pu (Fig. 1(b)) but with a larger overlapping of $f^{5/2}$ and $f^{7/2}$ subbands and the position of Fermi level a little deeper inside the $f^{5/2}$ band. This is an effect of a stronger hybridization of $5f$ orbitals with Co-d and Ga-p states in $PuCoGa_5$ comparing with metallic Pu.

The Coulomb interaction correction in LDA+U+SO calculations (Fig. 6(c) and (d)) results in a larger energy separation between $f^{5/2}$ and $f^{7/2}$ subbands (till 4 eV) and nearly pure orbital character of these bands, again very similar to metallic Pu (Fig. 1(d)). In Table IV (the second row corresponds to $PuCoGa_5$) the calculated values for spin, orbital and total moments are presented. Pu ion for our solution is predominantly in f^6 configuration but with

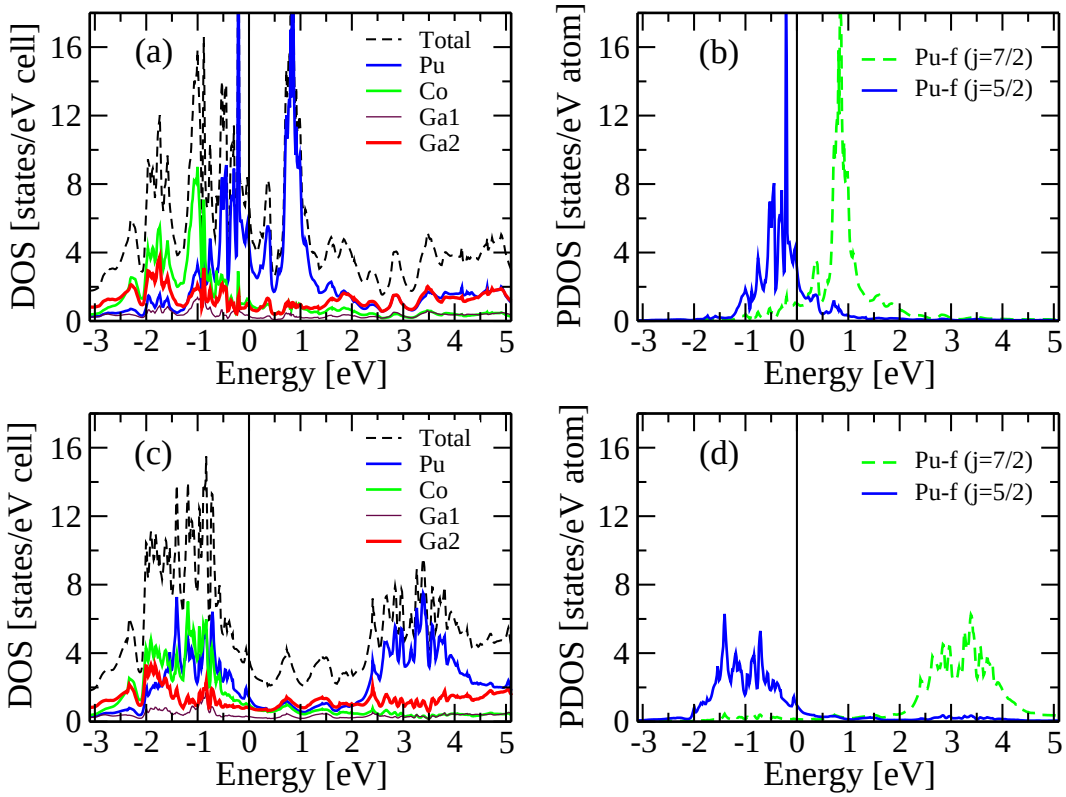

FIG. 7: (a) Total and partial densities of states of $PuCoGa_5$ calculated in LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for $PuCoGa_5$ from LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

a significant (18%) admixture of f^5 configuration. Sizable values of spin and orbital moment together with relatively small value of total moment gave similar to PuN case an intermediate coupling scheme closer to jj coupling.

We would like to note, that in spite of very similar to metallic Pu band structure for $5f$ states (compare Fig. 7(b) and Fig. 1(b)) in the LDA calculations, LDA+U+SO calculations scheme gave a magnetic ground state for $PuCoGa_5$ in agreement with experimental data.[82,86,87,88,89] In Table V (second row) the values of effective paramagnetic moments calculated using Eq. (14) are presented. The weighted value $\mu_{eff}^{calc} = 0.52\ \mu_B$ is smaller than experimental $\mu_{eff}^{exp} = 0.68\ \mu_B$, which is very close to the $\mu_{eff}^{jj} = 0.69\ \mu_B$ calculated with Lande g-factor g_{jj} obtained in jj coupling scheme.

C. $PuRh_2$

$PuRh_2$ crystallizes in Laves structure (C15) $a = 7.488$ Å.[98] From the magnetic susceptibility[98] $PuRh_2$ is a Curie-Weiss paramagnet with $p_{eff} = 0.88\ \mu_B$, $\Theta_p = -49$ K, and $\chi_{max} = 4.4 \times 10^{-3}$ emu mol^{-1}. Resistivity agrees well with the magnetic susceptibility results.[98] According to the specific heat results with $\gamma = 145$ mJ mol^{-1} K^{-2} and $\theta_D = 190$ K, $PuRh_2$ was classified as 'middle-weight' fermion system without temperature dependence of γ in the region of low temperatures.[99]

The dominant contribution to the $PuRh_2$ band structure gives a broad partially filled Rh-d band (Fig. 8(a)). Pu $5f$ states (Fig. 8(b)) show significant hybridization with Rh-d band. However the general feature common to metallic Pu and all Pu compounds investigated in this work, a separation into $f^{5/2}$ and $f^{7/2}$ subbands still can be seen here (Fig. 8(b)). The position of Fermi level inside the $f^{5/2}$ band similar to PuN case (Fig. 6(b)) shows that resulting configuration should be close to f^5. Indeed LDA+U+SO calculations gave (Fig. 8(c) and (d)) the $f^{5/2}$ states split into occupied and empty bands. In contrast to PuN case (Fig. 6(d)) empty $f^{5/2}$ band is not narrow but rather broad and has a two peak structure due to the strong hybridization with Rh-d states.

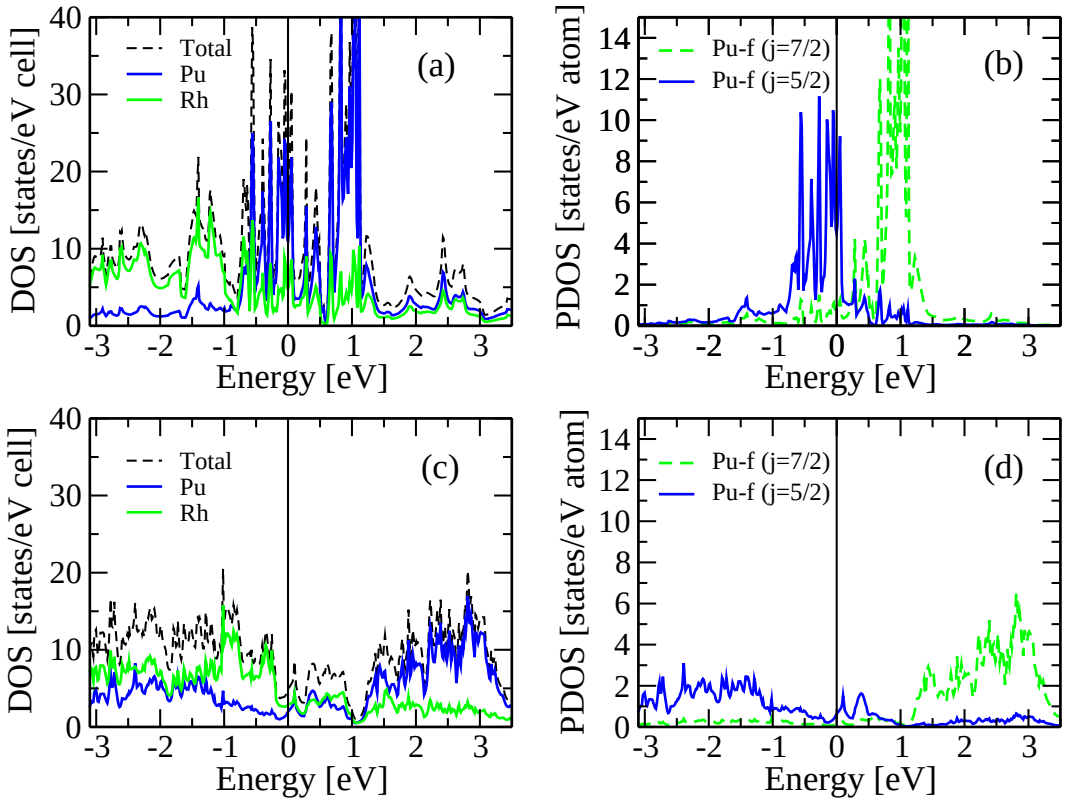

FIG. 8: (a) Total and partial densities of states of $PuRh_2$ calculated in LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for $PuRh_2$ from LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

In Table IV (the third row corresponds to $PuRh_2$) the calculated values for spin, orbital and total moments are presented. In agreement with the aforementioned density of states analysis, the Pu ion is predominantly in f^5 configuration with a significant admixture (25%) of f^6 configuration. A large values of spin moment results in intermediate coupling scheme closer to LS coupling. In Table V (third row) the values of effective paramagnetic moments calculated using Eq. (14) are presented. The weighted value $\mu_{eff}^{calc} = 1.27\ \mu_B$ is larger than experimental $\mu_{eff}^{exp} = 0.88\ \mu_B$ which still lies in the limits of $\mu_{eff}^{jj} = 1.99\ \mu_B$ and $\mu_{eff}^{LS} = 0.66\ \mu_B$ closer to LS coupling value μ_{eff}^{LS}.

D. $PuSi_2$

Structural and magnetic properties of $PuSi_2$ were reported by Boulet *et al.*[100] although this phase was earlier investigated in Ref. 101. This compound crystallizes in tetragonal $ThSi_2$-type (space group $I4_1/amd$) structure with $a = 3.9707(3)$ Å and $c = 13.6809(5)$ Å.[100] $PuSi_2$ susceptibility curve shows Curie-Weiss behavior[100,102] with $p_{eff} = 0.54\ \mu_B$, $\Theta_p = -58$ K, and $\chi_0 = 2.3 \times 10^{-5}$ emu mol^{-1} (Ref. 100). Almost field independent resistivity shows a broad maximum at 18 K suggesting strong spin fluctuations.[100]

The LDA band structure (Fig. 9(a)) shows a broad deep pseudogap with a very small density of states value on the Fermi level. This pseudogap separates $f^{5/2}$ and $f^{7/2}$ subbands (Fig. 9(b)) and position of the Fermi level exactly in the pseudogap gave a completely filled $f^{5/2}$ band and hence a pure f^6 configuration could be expected. Indeed LDA+U+SO calculations gave (Fig. 9(c) and (d)) a solution with the same type of band structure as without Coulomb interaction correction except increased energy separation between $f^{5/2}$ and $f^{7/2}$ subbands.

In Table IV (the fourth row corresponds to $PuSi_2$) the calculated values for spin, orbital and total moments are presented. Pu ion is in nearly pure f^6 configuration with a small (5%) contribution of f^5 configuration. Relatively small values of spin and orbital moments gave an intermediate coupling scheme very close to pure jj coupling. The weighted value of effective paramagnetic moment $\mu_{eff}^{calc} = 0.23\ \mu_B$ (Table V) is smaller than experimental $\mu_{eff}^{exp} =$

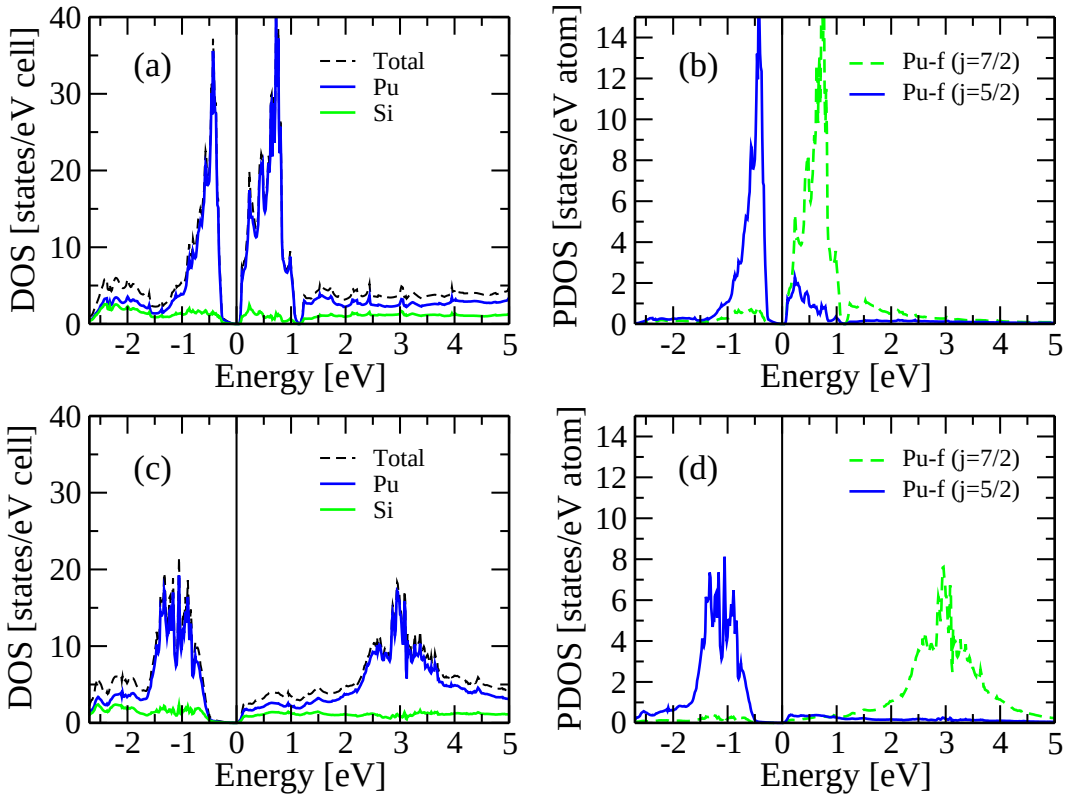

FIG. 9: (a) Total and partial densities of states of $PuSi_2$ calculated in LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for $PuSi_2$ from LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

0.54 μ_B.

E. PuTe

PuTe crystallizes in $NaCl$-type structure with $a = 6.183$ Å. Resistivity shows narrow-gap semiconductor behavior and an electronic specific heat coefficient has a high value $\gamma = 60$ mJ mol^{-1} K^{-2} (Ref. 103). In another work[104] the value of $\gamma = 30$ mJ mol^{-1} K^{-2} was reported. While formal valency of Pu in PuTe is equal +2, an intermediate valent Pu^{+2}-Pu^{+3} state in this compound was proposed.[105,106,107,108] Magnetic and optical properties of PuTe show a number of peculiarities.[109,110,111] A structural phase transition from NaCl to CsCl phase was proposed from resistivity measurements.[112]

Electronic structure of PuTe was calculated by Dirac equation-corrected ASA,[113] relativistic LAPW,[114] and LSDA augmented plane wave method (ASW).[115] From these calculation, $f^{7/2}$ and $f^{5/2}$ subbands are split on 1 eV[113] (or 0.3 eV in Ref. 114). Results strongly depend on spin-orbit coupling strength.[115] Based on the Mössbauer spectra results,[116] magnetic transition going from PuSb to PuTe with the vanishing of local moments was suggested.

Results of calculations by LDA and LDA+U+SO are presented in Fig. 10 and in Table IV (the fifth row corresponds to PuTe). The electronic structure and magnetic state are very similar to those for $PuSi_2$, only the pseudogap is not so well developed. Nearly pure f^6 configuration corresponds to the formal Pu valency +2 with a small values of magnetic moments described by 30% admixture of LS coupling to jj coupling scheme. The arguments against valency +2 in Ref. 105,106,107,108 were based on the very large ionic radius value for Pu^{+2} ion. However, in spite of the formal configuration f^6 in our results, the total number of $5f$ electrons is equal to 5.65 (effect of strong hybridization of $5f$orbitals with Sb-p states), which corresponds to the intermediate valency Pu^{+2}-Pu^{+3}. Another interesting fact is that going from PuTe to PuSb the number of $5f$ electrons decreases from 5.65 to 5.16, two times smaller than expected from formal valency difference. A very small value of magnetic moments obtained in our calculations (Table V) agrees well with nonmagnetic state of Pu ions in PuTe.[116]

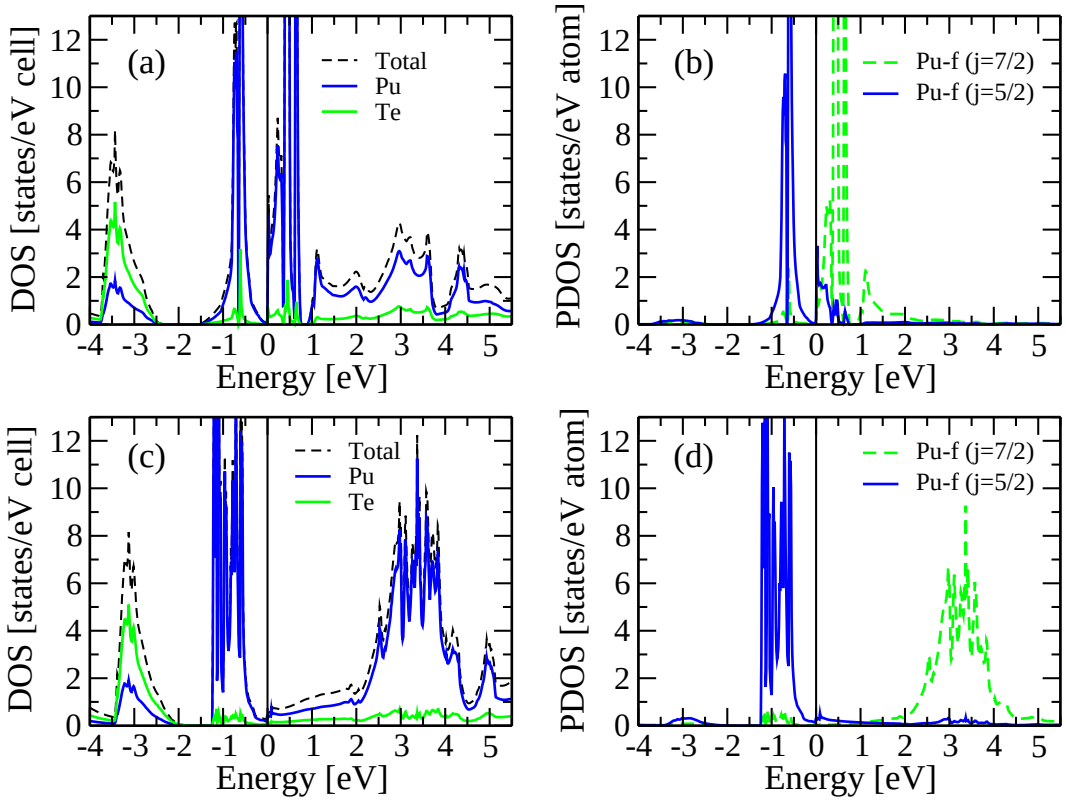

FIG. 10: (a) Total and partial densities of states of PuTe calculated in LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuTe from LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

F. PuSb

From magnetization measurements and neutron experiments an antiferromagnetic spin structure was found with a strong <001> anisotropy and ordering temperature 75 K.[117,118] Preferable intermediate coupling type closer to LS-type was proposed in Ref. 119 (model of wave function consisting of 90% LS- and 10 % jj-coupled wave functions[117] gave a possibility to AFM transition leaving strong anisotropy). Neutron-diffraction experiment reveals low-temperature Pu ion magnetic moment $\mu = 0.75\ \mu_B$ perpendicular to ferromagnetic (001) planes with Néel temperature $T_N = 85$ K and first-order transition to the incommensurate ferromagnetic phase.[109,119,120] Effective magnetic moment of paramagnetic phase from susceptibility was estimated as $\mu = 1.0\ \mu_B$.[121] Model of localized $5f$ electrons with weak hybridization to conducting electron states was proposed.[120,122] Electrical resistivity shows metallic behavior with Kondo-like broad maximum at 106 K.[123] X-ray photoelectron spectroscopy (XPS) and high-resolution valence-band ultraviolet photoelectron spectroscopy (UPS) showed strong localized nature of $5f$ Pu electrons in PuSb and pronounced f^5 configuration.[124]

Results of calculations by LDA and LDA+U+SO are presented in Fig. 11 and in Table IV (the sixth row corresponds to PuSb). The electronic structure and magnetic state are very similar to PuN, according to the formal valency +2 for Pu in both compounds.

We have calculated photoemission spectrum for PuSb (see Fig. 3). An agreement with experimental curve[125] is a good one. The main peak at ≈ 1.5 eV corresponding to Pu-$5f$ states (see Fig. 11(c)) is reproduced quite well.

In Table V (sixth row corresponds to PuSb) the values of effective paramagnetic moments calculated using Eq. (14) are presented. The calculated $\mu_{eff}^{calc} = 1.35\ \mu_B$ is close to experimental value $\mu_{eff}^{exp} = 1.00\ \mu_B$.

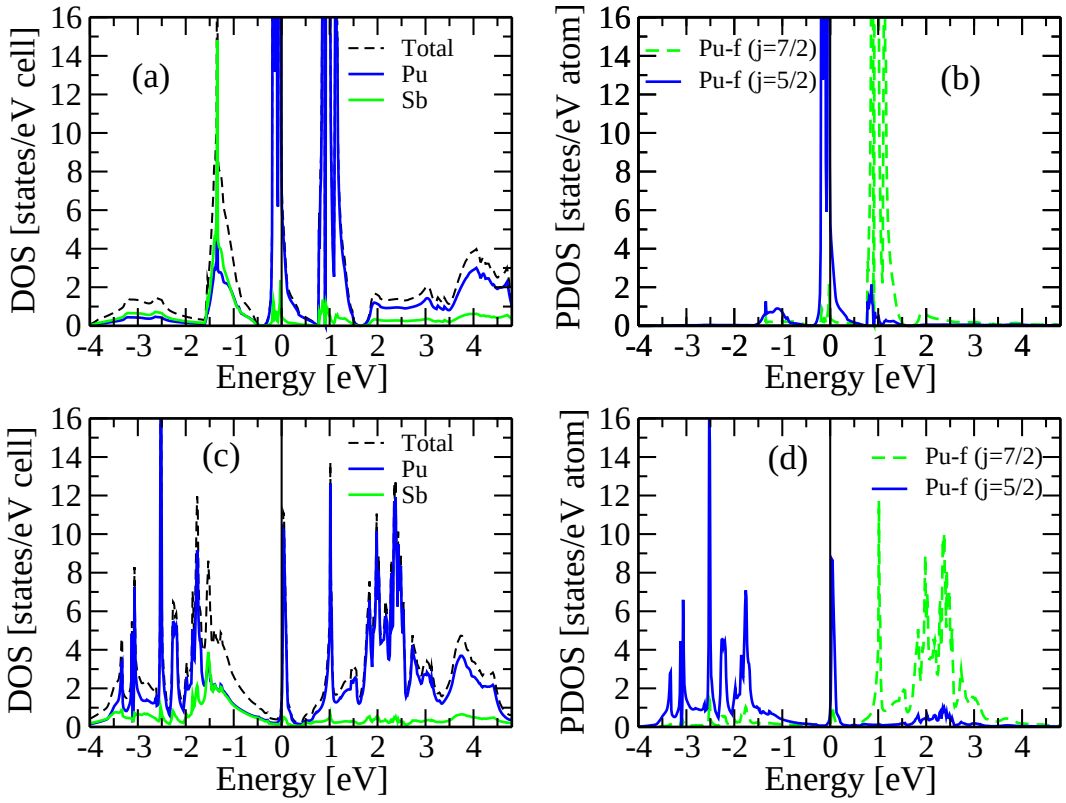

FIG. 11: (a) Total and partial densities of states of PuSb calculated in LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuSb from LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

V. CONCLUSION

In this work we present the results of theoretical investigation for Pu ion magnetic state in metallic plutonium and plutonium compounds. In contrast to all previous theoretical studies but in agreement with experimental measurements we have found for metallic Pu in both α and δ phases a nonmagnetic ground state with f^6 configuration of $5f$ shell in pure jj coupling scheme. A strong spin-orbit coupling for $5f$ electrons results in a splitting of f bands into well separated $f^{5/2}$ and $f^{7/2}$ subbands with $f^{5/2}$ band nearly fully occupied and $f^{7/2}$ band empty giving 'preformed' f^6 configuration. Taking into account Coulomb interaction via LDA+U potential does not change this nonmagnetic ground state.

We have shown that approximately equal strength of spin-orbit coupling and exchange interaction, whose matrices can not be made simultaneously diagonal in the same basis set, does not allow the use of the simplified diagonal forms of the corresponding Hamiltonian terms. That is true also for spin-polarized potential used in LSDA. Only a general non-diagonal matrix form of exchange interaction is appropriate for $5f$ electrons.

We have calculated also a series of plutonium compounds with different formal valency and the calculated magnetic moments values agree reasonably well with experimental data.

Comparison of the calculated and experimental photoemission spectra show that while LDA+U+SO method based on static mean-field approximation can reproduce Hubbard bands appearing in such strongly correlated materials as plutonium and its compounds, the quasiparticle peak on the Fermi energy can not be described by this method. The more elaborate Dynamical Mean-Field Theory (DMFT) is needed here. The results obtained in LDA+U+SO calculations could be used a basis for further DMFT studies.

VI. ACKNOWLEDGMENTS

The authors are indebted to A. I. Poteryaev, J. E. Medvedeva, and A. V. Kozhevnikov for contributing to the development of the LDA+U+SO code. This work was partly supported by the Russian Foundation for Basic Research grant RFFI-04-02-16096.

[1] *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic Press, New York, 1974), Vols. I and II.
[2] S. S. Hecker, D. R. Harbur, and T. G. Zocco, Prog. Mater. Sci. **49**, 429 (2004).
[3] G. H. Lander, Science **301**, 1057 (2003).
[4] *Challenges in Plutonium Science*, edited by N. G. Cooper, Los Alamos Sci. **26** (LANL, Los Alamos, NM, 2000).
[5] Current state of Pu problem is reviewed in Mat. Res. Soc. Bull. **26**, No. 9 (September), 2001; e.g., S. S. Hecker, *ibid.* **26**, 672 (2001).
[6] R. C. Albers, Nature **410**, 759 (2001).
[7] K. T. Moore, M. A. Wall, A. J. Schwartz, B. W. Chung, D. K. Shuh, R. K. Schulze, and J. G. Tobin, Phys. Rev. Lett. **90**, 196404 (2003); K. T. Moore, M. A. Wall, A. J. Schwartz, B. W. Chung, S. A. Morton, J. G. Tobin, S. Lazar, F. D. Tichelaar, H. W. Zandbergen, P. Söderlind, and G. van der Laan, Philos. Mag. **84**, 1039 (2004).
[8] G. van der Laan, K. T. Moore, J. G. Tobin, B. W. Chung, M. A. Wall, and A. J. Schwartz, Phys. Rev. Lett. **93**, 097401 (2004); G. var der Laan and B. T. Thole, Phys. Rev. B **53**, 14458 (1996).
[9] B. R. Cooper, R. Siemann, D. Yang, P. Thayamballi, and A. Banerjea, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (Elsevier, Amsterdam, 1985), Vol. 6, p. 435.
[10] A. J. Arko, J. J. Joyce, L. A. Morales, J. H. Terry, and R. K. Schulze, Los Alamos Sci. **26**, 168 (2000).
[11] A. J. Arko, J. J. Joyce, L. Morales, J. Wills, J. Lashley, F. Wastin, and J. Rebizant, Phys. Rev. B **62**, 1773 (2000); J. Terry, R. K. Schulze, J. D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, D. K. Shuh, G. van der Laan, D. A. Arena, and J. G. Tobin, Surf. Sci. **499**, L141 (2002).
[12] J. R. Naegele, L. Manes, J. C. Spirlet, and W. Müller, Phys. Rev. Lett. **52**, 1834 (1986); J. R. Naegele, J. Ghijsen, and L. Manes, *Actinides – Chemistry and Physical Properties, Structure and Bounding 59/60* (Springer-Verlag, Berlin, 1985), p. 197.
[13] L. Havela, T. Gouder, F. Wastin, and J. Rebizant, Phys. Rev. B **65**, 235118 (2002).
[14] J. G. Tobin, B. W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G. D. Waddill, and G. van der Laan, Phys. Rev. B **68**, 155109 (2003).
[15] *Plutonium Handbook: a Guide to the Technology*, edited by O. J. Wick (American Nuclear Society, LaGrange Park, IL, 1980).
[16] J. C. Lashley, J. Singleton, A. Migliori, J. B. Betts, R. A. Fisher, J. L. Smith, and R. J. McQueeney, Phys. Rev. Lett. **91**, 205901 (2003).
[17] J. Wong, M. Krisch, D. L. Farber, F. Occelli, A. J. Schwartz, T.-C. Chiang, M. Wall, C. Boro, and R. Xu, Science **301**, 1078 (2003).
[18] H. M. Ledbetter and R. L. Moment, Acta Metall. **24**, 891 (1976).
[19] Recently, this effect of softening was found from inelastic neutron scattering on polycrystals of δ phase $^{242}Pu_{0.95}Al_{0.05}$ by another experimental group: R. J. McQueeney, A. C. Lawson, A. Migliori, T. M. Kelley, B. Filtz, M. Ramos, B. Martinez, J. C. Lashley, and S. V. Vogel, Phys. Rev. Lett. **92**, 146401 (2004).
[20] X. Dai, S. Y. Savrasov, G. Kotliar, A. Migliori, H. Ledbetter, and E. Abrahams, Science **300**, 953 (2003).
[21] J. C. Lashley, A. C. Lawson, R. J. McQueeney, and G. H. Lander, cond-mat/0410634.
[22] For a review and further references, see M. Richter, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 2001), Vol. 13, p. 87.
[23] J. van Ek, P. A. Sterne, and A. Gonis, Phys. Rev. B **48**, 16280 (1993).
[24] P. Söderlind, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **55**, 1997 (1997).
[25] M. D. Jones, J. C. Boettger, R. C. Albers, and D. J. Singh, Phys. Rev. B **61**, 4644 (2000). For the calculations of other plutonium phases with FLAPW-GGA method, see, P. Söderlind, Adv. Phys. **47**, 959 (1998); P. Söderlind and B. Sadigh, Phys. Rev. Lett. **92**, 185702 (2004); G. Robert, A. Pasturel, and B. Siberchicot, J. Phys.: Condens. Matter **15**, 8377 (2003); B. Sadigh, P. Söderlind, and W. G. Wolfer, Phys. Rev. B **68**, 241101(R) (2003). VASP code was used by J. Bouchet, R. C. Albers, M. D. Jones, and G. Jomard, Phys. Rev. Lett. **92**, 095503 (2004).
[26] P. Söderlind, O. Eriksson, B. Johansson, and J. M. Wills, Phys. Rev. B **50**, 7291 (1994); J. M. Wills and O. Eriksson, *ibid.* **45**, 13879 (1992).
[27] G. W. Fernando, E. H. Sevilla, and B. R. Cooper, Phys. Rev. B **61**, 12562 (2000).
[28] L. Nordström, J. M. Wills, P. H. Andersson, P. Söderlind, and O. Eriksson, Phys. Rev. B **63**, 035103 (2001).
[29] For the review, see *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation*, edited by V. I. Anisimov (Gordon and Breach Science Publishers, Amsterdam, 2000); V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
[30] S. Y. Savrasov and G. Kotliar, Phys. Rev. Lett. **84**, 3670 (2000).

[31] *Plutonium – A General Servey*, edited by K. H. Lieser (Verlag, Chemie, 1974).
[32] The set of Slater integrals $F^{(2)} = 10$ eV, $F^{(4)} = 7$ eV, and $F^{(6)} = 5$ eV used in Ref. 30 leads to Hund exchange parameter $J_H = 0.85$ eV according to the standard formula $J_H = (286F^{(2)} + 195F^{(4)} + 250F^{(6)})/6435$ for f elements.
[33] J. Bouchet, B. Siberchicot, F. Jollet, and A. Pasturel, J. Phys.: Condens. Matter **12**, 1723 (2000).
[34] P. Söderlind, A. L. Landa, and B. Sadigh, Phys. Rev. B **66**, 205109 (2002).
[35] P. Söderlind, Europhys. Lett. **55**, 525 (2001).
[36] Y. Wang and Y. Sun, J. Phys.: Condens. Matter **12**, L311 (2000).
[37] A. V. Postnikov and V. P. Antropov, Comp. Mat. Sci. **17**, 438 (2000).
[38] I. V. Solovyev, A. I. Liechtenstein, V. A. Gubanov, V. P. Antropov, and O. K. Andersen, Phys. Rev. B **43**, 14414 (1991); M. I. Katsnelson, I. V. Solovyev, and A. V. Trefilov, JETP Lett. **56**, 272 (1992).
[39] M. Pénicaud, J. Phys.: Condens. Matter **9**, 6341 (1997).
[40] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer, Boston, 1994).
[41] A. L. Kutepov and S. G. Kutepova, J. Phys.: Condens. Matter **15**, 2607 (2003). Compare with X. Wu and A. K. Ray, cond-mat/0407676.
[42] A. L. Kutepov and S. G. Kutepova, J. Magn. Magn. Mater. **272-276**, e329 (2004).
[43] O. Eriksson, J. D. Becker, A. V. Balatsky, and J. M. Wills, J. Alloys Comp. **287**, 1 (1999). See also B. R. Cooper, O. Vogt, Q.-G. Sheng, and Y.-L. Lin, Philos. Mag. B **79**, 683 (1999).
[44] L. Petit, A. Svane, Z. Szotek, P. Strange, H. Winter, and W. M. Temmerman, J. Phys.: Condens. Matter **13**, 8697 (2001); L. Petit, A. Svane, W. M. Temmerman, and Z. Szotek, Solid State Commun. **116**, 379 (2000).
[45] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[46] W. M. Temmerman, A. Svane, Z. Szotek, and H. Winter, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998), p. 327.
[47] L. Petit, A. Svane, Z. Szotek, and W. M. Temmerman, Mol. Phys. Rep. **38**, 20 (2003).
[48] L. Petit, A. Svane, Z. Szotek, and W. M. Temmerman, Mat. Res. Soc. Symp. Proc. **802**, DD6.7.1 (2004).
[49] L. Petit, A. Svane, W. M. Temmerman, and Z. Szotek, J. Eur. Phys. B **25**, 139 (2002).
[50] L. Petit, A. Svane, and W. M. Temmerman, Science **301**, 498 (2003).
[51] A. M. N. Niklasson, J. M. Wills, M. I. Katsnelson, I. A. Abrikosov, O. Eriksson, and B. Johansson, Phys. Rev. B **67**, 235105 (2003).
[52] J. M. Wills, O. Eriksson, A. Delin, P. H. Andersson, J. J. Joyce, T. Durakiewicz, M. T. Butterfield, A. J. Arko, D. P. Moore, and L. A. Morales, J. Elec. Spectrosc. Rel. Phen. **135**, 163 (2004).
[53] G. Kotliar and D. Vollhardt, Phys. Today **57**, No. 3 (March), 53 (2004).
[54] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[55] A. Georges, AIP Conf. Proc. **715**, 3 (2004); G. Kotliar and S. Y. Savrasov, in *New Theoretical Approaches to Strongly Correlated Systems*, edited by A. M. Tsvelik (Kluwer Academic Publishers, The Netherlands, 2001), p.259.
[56] V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, J. Phys.: Condens. Matter **9**, 7359 (1997).
[57] K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Blümer, A. K. McMahan, R. T. Scalettar, Th. Pruschke, V. I. Anisimov, and D. Vollhardt, *Psi-k Newsletter* **56**, 65 (2003); D. Vollhardt, K. Held, G. Keller, R. Bulla, Th. Pruschke, I. A. Nekrasov, and V. I. Anisimov, cond-mat/0408266.
[58] S. Y. Savrasov and G. Kotliar, Phys. Rev. B **69**, 245101 (2004); G. Kotliar and S. Y. Savrasov, Int. J. Mod. Phys. B **17**, 5101 (2003).
[59] S. Y. Savrasov, G. Kotliar, and E. Abrahams, Nature **410**, 793 (2001). For the details of this calculation and comprehensive review of the method, see Ref. 58.
[60] B. Johansson and M. S. S. Brooks, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (Elsevier, Amsterdam, 1993), Vol. 17, p. 149; U. Benedict and W. B. Holzapfel, *ibid.*, Vol. 17, p. 245.
[61] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).
[62] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); O. Gunnarsson, O. Jepsen, and O. K. Andersen, Phys. Rev. B **27**, 7144 (1983).
[63] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).
[64] V. I. Anisimov and O. Gunnarsson, Phys. Rev. B **43**, 7570 (1991).
[65] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Pergamon, Oxford, 1965).
[66] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
[67] U. von Barth and L. Hedin, J. Phys. C: Solid State Phys. **5**, 1629 (1972).
[68] For a comprehensive review of noncollinear magnetic calculations, see L. M. Sandratskii, Adv. Phys. **47**, 91 (1998).
[69] J. Kübler, K.-H. Höck, J. Sticht, and A. R. Williams, J. Phys. F: Met. Phys. **18**, 469 (1988).
[70] L. Nordström and D. J. Singh, Phys. Rev. Lett. **76**, 4420 (1996).
[71] D. A. Young, *Phase diagram of the Elements* (University of California Press, Berkley, 1991).
[72] P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai, Phys. Rev. Lett. **53**, 2512 (1984).
[73] J. P. Desclaux and A. J. Freeman, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (Elsevier, Amsterdam, 1984), Vol. 1.
[74] P. E. A. Turchi, A. Gonis, N. Kioussis, D. L. Price, and B. R. Cooper, in *Electron Correlations and Materials Properties*, edited by A. Gonis, N. Kioussis, and M. Ciftan (Kluwer Academic, New York, 1999), p. 531.
[75] Vectors of spin **S** and orbital **L** moments have opposite directions so that total moments value is calculated via $J = |L - S|$.

[76] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).
[77] F. Anselin, J. Nucl. Mater. **10**, 331 (1963).
[78] A. Boeuf, R. Cacciuffo, J. M. Fournier, L. Manes, J. Rebizant, E. Roudaut, and F. Rustichelli, Solid State Commun. **52**, 451 (1984). See also P. Burlet, J. M. Fournier, L. Manes, J. Rebizant, and F. Rustichelli, Proc. of Iliémes Jounées des Actinides, edited by G. Bombieri (Venice, Italy, 1982).
[79] D. J. Martin, R. D. A. Hall, J. A. Lee, M. J. Mortimer, and P. W. Sutcliffe, Harwell AERE Rep. **76**, 12599 (1976).
[80] G. Raphaël and C. H. de Novion, Solid State Commun. **7**, 791 (1969).
[81] M. S. S. Brooks, J. Phys. F: Met. Phys. **14**, 857 (1984).
[82] J. L. Sarrao, L. A. Morales, J. D. Thompson, B. L. Scott, G. R. Stewart, F. Wastin, J. Rebizant, P. Boulet, E. Colineau, and G. H. Lander, Nature **420**, 297 (2002).
[83] I. Opahle, S. Elgazzar, K. Koepernik, and P. M. Oppeneer, Phys. Rev. B **70**, 104504 (2004).
[84] H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson, Phys. Rev. Lett. **84**, 4986 (2000); C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, Z. Fisk, and P. Monthoux, J. Phys.: Condens. Matter **13**, L337 (2001); C. Petrovic, R. Movshovich, M. Jaime, P. G. Pagliuso, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson, Europhys. Lett. **53**, 354 (2001).
[85] M. F. Hundley, A. Malinowski, P. G. Pagliuso, J. L. Sarrao, and J. D. Thompson, Phys. Rev. B **70**, 035113 (2004).
[86] J. L. Sarrao, J. D. Thompson, N. O. Moreno, L. A. Morales, F. Wastin, J. Rebizant, P. Boulet, E. Colineau, and G. H. Lander, J. Phys.: Condens. Matter **15**, S2275 (2003).
[87] J. D. Thompson, J. L. Sarrao, L. A. Morales, F. Wastin, and P. Boulet, Physica C **412-414**, 10 (2004).
[88] J.-C. Griveau, C. Pfleiderer, P. Boulet, J. Rebizant, and F. Wastin, J. Magn. Magn. Mater. **272-276**, 154 (2004).
[89] Y. Bang, A. V. Balatsky, F. Wastin, and J. D. Thompson, Phys. Rev. B **70**, 104512 (2004).
[90] E. D. Bauer, J. D. Thompson, J. L. Sarrao, L. A. Morales, F. Wastin, J. Rebizant, J. C. Griveau, P. Javorsky, P. Boulet, E. Colineau, G. H. Lander, and G. R. Stewart, Phys. Rev. Lett. **93**, 147005 (2004).
[91] K. Tanaka, H. Ikeda, and K. Yamada, cond-mat/0403069.
[92] F. Wastin, P. Boulet, J. Rebizant, E. Colineau, and G. H. Lander, J. Phys.: Condens. Matter **15**, S2279 (2003).
[93] I. Opahle and P. M. Oppeneer, Phys. Rev. Lett. **90**, 157001 (2003).
[94] A. Szajek and J. A. Morkowski, J. Phys.: Condens. Matter **15**, L155 (2003).
[95] T. Maehira, T. Hotta, K. Ueda, and A. Hasegawa, Phys. Rev. Lett. **90**, 207007 (2003); cond-mat/0212033.
[96] T. Hotta and K. Ueda, Phys. Rev. B **67**, 104518 (2003).
[97] P. Söderlind, Phys. Rev. B **70**, 094515 (2004).
[98] A. R. Harvey, M. B. Brodsky, and W. J. Nellis, Phys. Rev. B **7**, 4137 (1973).
[99] G. R. Stewart, B. Andraka, and R. G. Haire, J. Alloys Comp. **213**, 111 (1994).
[100] P. Boulet, F. Wastin, E. Colineau, J. C. Griveau, and J. Rebizant, J. Phys.: Condens. Matter **15**, S2305 (2003).
[101] W. H. Zachariasen, Acta Crystallogr. **2**, 94 (1949); C. C. Land, K. A. Johnson, and F. H. Ellinger, J. Nucl. Mater. **15**, 23 (1965).
[102] S. E. Olsen, J. Appl. Phys. **31**, 340 (1960).
[103] J. M. Fournier, E. Pleska, J. Chiapusio, J. Rossat-Mignod, J. Rebizant, J. C. Spirlet, and O. Vogt, Physica B **163**, 493 (1990).
[104] G. R. Stewart, R. G. Haire, J. C. Spirlet, and J. Rebizant, J. Alloys Comp. **177**, 167 (1991).
[105] G. H. Lander, M. Wulff, J. Rebizant, J. C. Spirlet, P. J. Brown, and O. Vogt, J. Appl. Phys. **63**, 3601 (1988).
[106] P. Wachter, F. Marabelli, and B. Bucher, Phys. Rev. B **43**, 11136 (1991).
[107] M. Mendik, P. Wachter, J. C. Spirlet, and J. Rebizant, Physica B **186-188**, 678 (1993).
[108] P. Wachter, Solid State Commun. **127**, 599 (2003).
[109] P. Burlet, S. Quezel, J. Rossat-Mignod, J. C. Spirlet, J. Rebizant, and O. Vogt, Physica B **159**, 129 (1989); G. H. Lander, J. Rebizant, J. C. Spirlet, A. Delapalme, P. J. Brown, O. Vogt, and K. Mattenberger, Physica B **146**, 341 (1987).
[110] C. E. Olsen, A. L. Comstock, and Th. A. Sandenaw, J. Nucl. Mater. **195**, 312 (1992).
[111] C. Abraham, U. Benedict, and J. C. Spirlet, Physica B **222**, 52 (1996).
[112] V. Ichas, J. C. Griveau, J. Rebizant, and J. C. Spirlet, Phys. Rev. B **63**, 045109 (2001).
[113] M. S. S. Brooks, J. Magn. Magn. Mater. **63-64**, 649 (1987).
[114] A. Hasegawa and H. Yamagami, J. Magn. Magn. Mater. **104-107**, 65 (1992).
[115] P. M. Oppeneer, T. Kraft, and M. S. S. Brooks, Phys. Rev. B **61**, 12825 (2000).
[116] J. P. Sanchez, J. C. Spirlet, J. Rebizant, and O. Vogt, J. Magn. Magn. Mater. **63-64**, 139 (1987).
[117] B. R. Cooper, P. Thayamballi, J. C. Spirlet, W. Müller, and O. Vogt, Phys. Rev. Lett. **51**, 2418 (1983); G. H. Lander, A. Delapalme, P. J. Brown, J. C. Spirlet, J. Rebizant, and O. Vogt, J. Appl. Phys. **57**, 3748 (1985).
[118] G. H. Lander, A. Delapalme, P. J. Brown, J. C. Spirlet, J. Rebizant, and O. Vogt, Phys. Rev. Lett. **53**, 2262 (1984).
[119] P. Burlet, S. Quezel, J. Rossat-Mignod, J. C. Spirlet, J. Rebizant, W. Müller, and O. Vogt, Phys. Rev. B **30**, 6660 (1984); P. Burlet, J. Rossat-Mignod, G. H. Lander, J. C. Spirlet, J. Rebizant, and O. Vogt, *ibid.* **36**, 5306 (1987).
[120] G. H. Lander, W. G. Stirling, J. Rossat-Mignod, J. C. Spirlet, J. Rebizant, and O. Vogt, Physica B **136**, 409 (1986).
[121] J. C. Spirlet, J. Rebizant, and O. Vogt, in Treizième Journèe des Actinides, Elat, Israel, 1983 (unpublished).
[122] G. J. Hu, N. Kioussis, B. R. Cooper, and A. Banerjea, J. Appl. Phys. **61**, 3385 (1987).
[123] A. Blaise, J. M. Collard, J. M. Fournier, J. Rebizant, J. C. Spirlet, and O. Vogt, Physica B **130**, 99 (1985).
[124] T. Gouder, F. Wastin, J. Rebizant, and L. Havela, Phys. Rev. Lett. **84**, 3378 (2000).
[125] T. Durakiewicz, J. J. Joyce, G. H. Lander, C. G. Olson, M. T. Butterfield, E. Guziewicz, A. J. Arko, L. Morales, J. Rebizant, K. Mattenberger, and O. Vogt, Phys. Rev. B **70**, 205103 (2004).